

**STUDIES TOWARDS THE DEVELOPMENT OF  
NEW CATALYSTS FOR METHANE CONVERSION**

Thesis by

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## ABSTRACT

In efforts to develop new catalysts for the partial oxidation of methane to methanol, studies were focused on developing supported aqueous phase (SAP) catalysts for this chemistry. The work can be separated into two main projects. First, steps were taken to prepare an organometallic SAP catalyst. A water-soluble sulfonated Pt diimine species has been prepared and supported on controlled-pore glass. The compound was characterized by solid state  $^{13}\text{C}$  CP-MAS NMR, and observations were made on the compounds behavior. This work is carried out in collaboration with research into homogeneous organometallic catalysts, and progress in this area is dependent on the development of successful homogeneous catalysts. The second project involves using platinum/copper salt catalyst for the hydroxylation of alkanes, where dioxygen is the ultimate oxidant. Several homogeneous reactions were carried out to investigate the reactivity of this catalyst system in solution. The catalysts were found to successfully hydroxylate sulfonated alkanes as well as ethane and methane, all with multiple platinum turnovers. Product characterizations were carried out using  $^1\text{H}$  NMR and GC/MS. Efforts were also begun to develop a SAP catalyst with the Pt/Cu system, modeled after the SAP Pd/Cu Wacker oxidation catalyst.

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## 1. INTRODUCTION TO METHANE CONVERSION

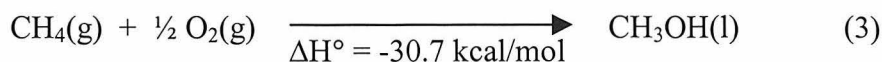
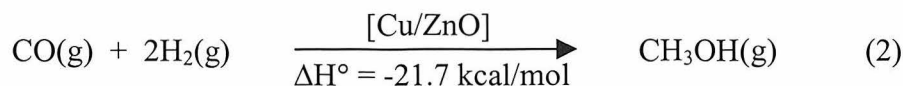
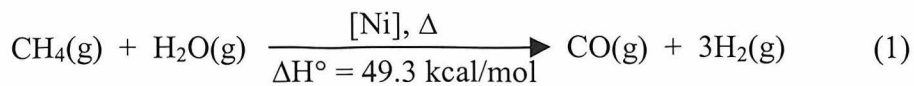
Issues of fuel supply, usage and the resulting environmental impact have been a major political and economical concern and the topic of hot debate and intense scientific study for many years. The use of coal and fossil fuels has become much less attractive from most standpoints, and much effort has been directed at discovery and utilizing natural and cleaner sources of fuel. Many would like to shift even further into using solar, water and even wind power. Currently, alkanes are the most abundant and least expensive hydrocarbon feedstocks available.<sup>1</sup> With plentiful and global gas supply sources, BP foresees natural gas, or methane, as the principal fuel for power and refineries building desired products starting with a methane feedstock.<sup>2</sup>

From an environmental standpoint, natural gas is a very attractive alternative. It is a clean burning fuel, giving off lower CO<sub>2</sub> emissions due to its higher H/C ratio compared to other hydrocarbon feedstocks.<sup>2</sup> Sulfur has long been a major problem in the use of fossil fuels, but since sulfur is removed at extraction and processing stages, SO<sub>2</sub> emissions are negligible.<sup>2</sup> Natural gas can be burned with a uniform and controlled flame temperature, which results in lower NO<sub>x</sub> emissions.<sup>2</sup> Greenhouse gas emission levels would also be lowered by using natural gas as fuel for power generation, transportation, and chemical feedstocks.<sup>2</sup> Compared to using coal power, the use of natural gas would also have lower emissions of other pollutants, such as ash and particulates, mercury and other metals, solid waste and process water.<sup>2</sup>

There is an enormous supply of natural gas around the world. As of 1998, there were 5180 trillion cubic feet of proven total global gas reserves.<sup>2</sup> The energy content of these reserves is approximately the same as all the current volumes of discovered oil.<sup>2</sup> At current consumption rates, this known supply of natural gas is enough to last 200 years.<sup>2</sup> Furthermore, no real effort has been put into exploration for gas reserves, so there are potentially many more reserves, making the total supply much larger.<sup>2</sup>

Industrial efforts in the area of natural gas are focusing on the delivery of gas to markets and the globalization of gas.<sup>2</sup> BP would like to lower the cost of supplying gas in order to improve the flexibility and scale with which the gas supplies can be brought to new and existing markets.<sup>2</sup> Technologies are also being developed to use natural gas in both traditional and non-traditional markets, including power and heat, transportation and chemical feedstocks.<sup>2</sup>

Obviously methane, and other alkanes, are an important potential feedstock, but to really make the most efficient use of alkanes, they must be converted to more valuable products. Unfortunately, alkanes are quite unreactive and currently have limited use as starting materials because few methods exist for the selective conversion of alkanes to desired products.<sup>1</sup> Several desired reactions are thermodynamically unfavorable at reasonable temperatures and transformations that do take place are often inefficient.<sup>1</sup> For example, steam reforming of methane is used to generate synthesis gas,  $\text{CO} + \text{H}_2$ , as shown in Equation (1).<sup>1</sup> Synthesis gas is used directly in some industrial reactions but is often converted into methanol for use as fuel or as a chemical feedstock, Equation (2).<sup>1</sup> Direct oxidation of methane would be a much more efficient way to generate methanol, as shown in Equation (3).<sup>1</sup>



The direct oxidation of methane to methanol would be an enormously valuable reaction, but there are many challenges facing this reaction chemistry. There is the difficulties of unreactivity and low efficiency, but selectivity is truly the biggest challenge.<sup>1</sup> Many reactions lead to overoxidation, producing CO<sub>2</sub> and H<sub>2</sub>O.<sup>1</sup> There are organometallic catalytic compounds that can address the selectivity concern, but they are often too sensitive to the oxidants used in the reaction and are therefore unusable.<sup>1</sup> As yet, there are no catalysts capable of carrying out this reaction with in a cost efficient way.

The topic of the research covered in this thesis has been the development of catalysts for the partial oxidation of methane to methanol. There is much research going on in this area, and the efforts of this work are focused on investigating some new catalyst systems to determine their potential as alkane hydroxylation catalysts.

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2. The Gas Economy. <http://www.bpgaseconomy.com> (accessed May 2002), path: About the Gas Economy.

## 2. SUPPORTED AQUEOUS PHASE CATALYSTS FOR METHANE CONVERSION

### INTRODUCTION

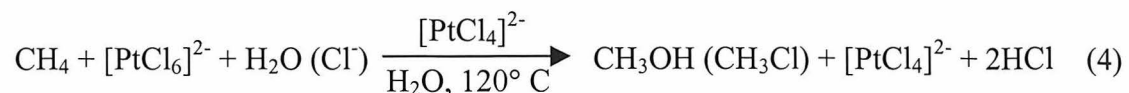
Homogeneous catalytic processes continue to provide a wealth of new and interesting reaction chemistries, and as a result, this area of chemistry has and continues to be widely studied and to grow rapidly. This growth is due to the industrially valuable advantages of the attainable activities and selectivities.<sup>1</sup> Homogeneous processes also operate efficiently under relatively mild conditions, with few by-products.<sup>1</sup> It is no surprise the problem of alkane oxidation is being tackled by catalyst systems in homogeneous solutions.

Current research addresses homogeneous alkane oxidation by electrophilic late transition metals ions, specifically Pt(II).<sup>2</sup> This type of system is robust and has shown unusual selectivities, and therefore, could prove to be a practical approach for selective alkane conversion.<sup>2</sup> Two major problems hinder attempts to selectively oxidize alkanes: chemoselectivity, where the products of oxidation are more reactive than the alkane substrate, and regioselectivity, making attack on primary C-H bonds difficult.<sup>2</sup> However, studies have shown that with a homogeneous organometallic system, these selectivity issues could be overcome.<sup>2</sup> It has been shown that strong C-H bonds can be activated selectively in the presence of weaker ones, and there are examples of organometallic



alkane C-H activations with reversed regioselectivities, where the primary C-H bonds are actually preferred.<sup>2</sup>

In the early seventies, Shilov and co-workers reported the use of a Pt(II)/Pt(IV) system in aqueous solution to generate oxidized alkane products, RCl and ROH, from reaction with methane.<sup>2</sup> The reaction is shown in Equation (4)<sup>2</sup>:



This system was found to be very robust, being neither air- or water-sensitive, and possessed the desired reversed regioselectivity.<sup>2</sup> In 1983, Shilov and co-workers proposed a mechanism and catalytic cycle for platinum-catalyzed alkane oxidation, as shown in Figure 2.1.<sup>2</sup>

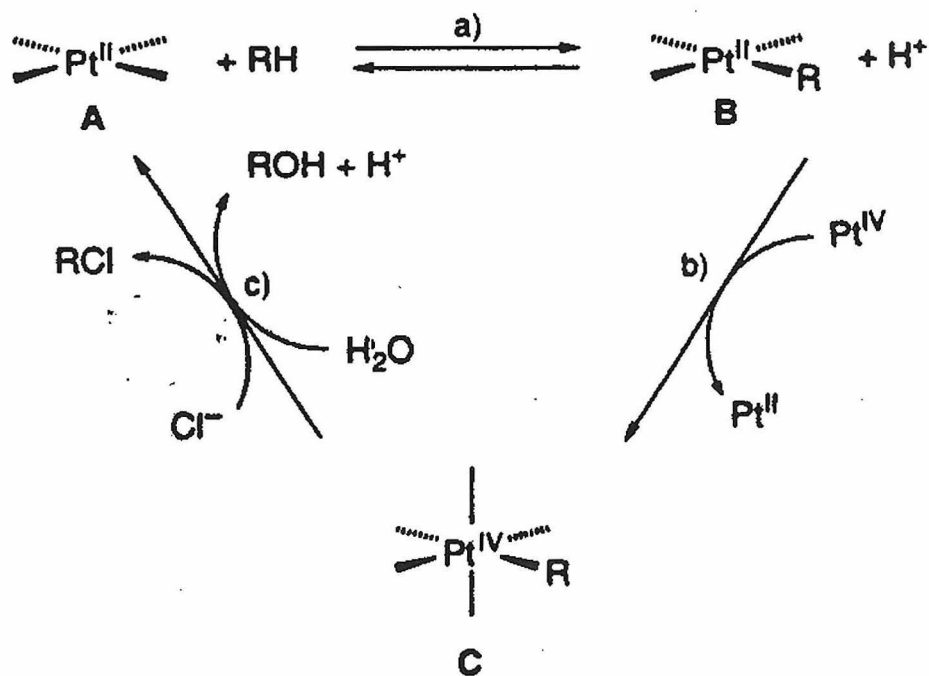


Figure 2.1.<sup>2</sup> Proposed catalytic cycle for platinum-catalyzed alkane oxidation.

According to the proposed mechanism, alkane conversion occurs by three basic steps, as shown in Figure 2.1. The first step, a), consists of an electrophilic activation of the alkane by platinum(II), generating an alkylplatinum(II) intermediate.<sup>2</sup> This step appears to be the rate- and selectivity-determining step.<sup>2</sup> The second step, b), is the oxidation of the alkylplatinum(II) intermediate to an alkylplatinum(IV) intermediate.<sup>2</sup> The oxidation is believed to occur by a direct two-electron transfer from the intermediate to the Pt(IV) species,  $[\text{PtCl}_6]^{2-}$ .<sup>2</sup> The third step, c), is the reductive elimination of the oxidized alkane product from the alkylplatinum(IV) species, regenerating the Pt(II) catalyst.<sup>2</sup> This mechanism has been the subject of much study, and over the years features of individual steps have been identified, and the mechanistic picture has become much clearer.<sup>2</sup> With this growing understanding, new possibilities are becoming evident, especially the development of new catalysts and the use of less expensive oxidants, such as  $\text{O}_2$ , in exchange for Pt(IV).<sup>2</sup>

Despite the many advantages of homogeneous catalysis, there are disadvantages as well. Of extreme industrial importance, homogeneous catalysis makes catalyst recovery and product separation extremely difficult.<sup>1</sup> Furthermore, and with particular relevance to the project at hand, methane solubility is very low in most common solvents.

A possible solution to these difficulties would be to immobilize the catalytic species while retaining the structure and properties of the species in solution. Perhaps the most promising method of immobilization is the dissolution of the catalytic complex in a nonvolatile solvent which is adsorbed onto a support.<sup>1</sup> Catalysts made this way make up the class of heterogeneous catalysts called supported aqueous-phase (SAP) catalysts (Figure 2.2).<sup>1,3</sup> The SAP catalyst consists of a water-soluble transition metal complex in

an aqueous layer which is immobilized in the pores of a high surface-area, hydrophilic solid.<sup>1,3</sup> This system maintains the catalyst in the aqueous phase, which is immiscible with the organic reactant and product phase.<sup>1,3</sup>

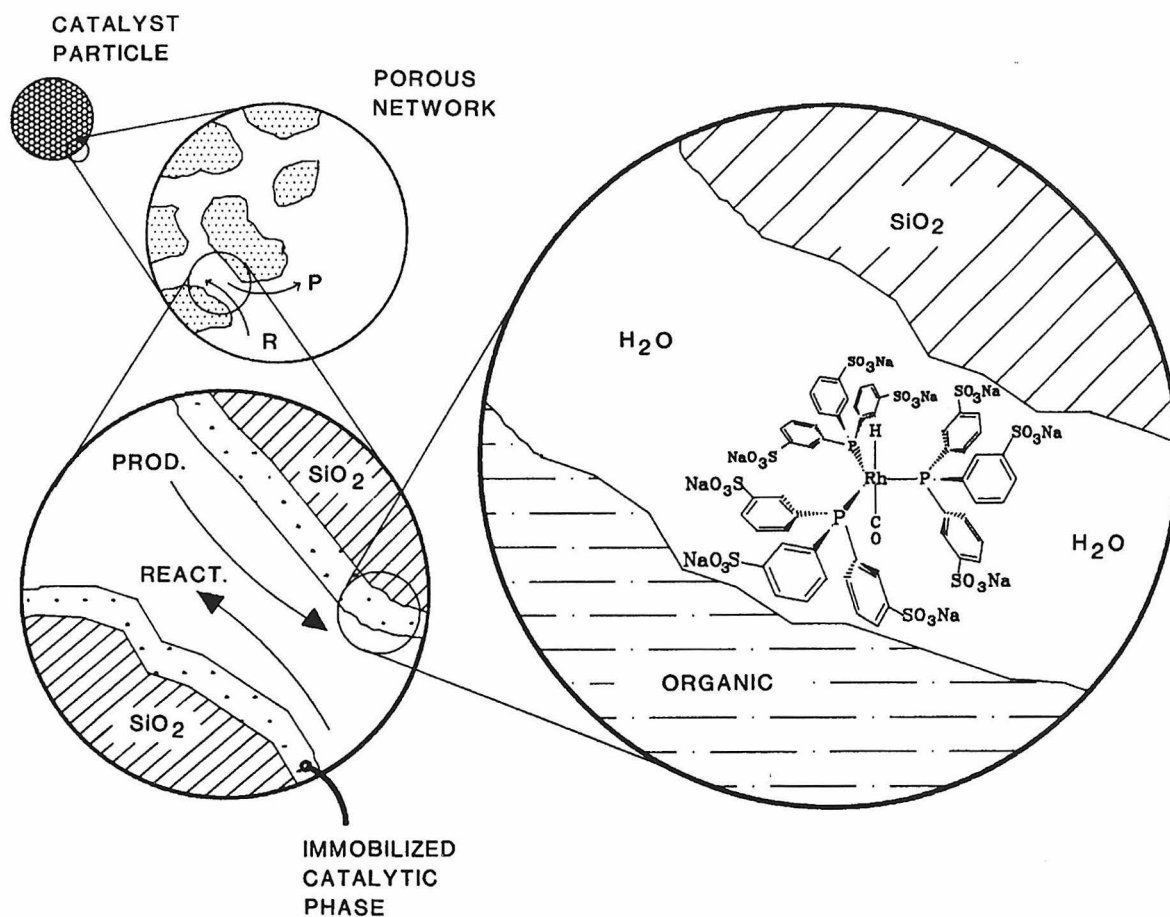


Figure 2.2.<sup>1</sup> Schematic representation of a SAP catalyst system.

There are many advantages to the SAP catalyst system. As mentioned previously, the catalyst species is separate from the reactant and product phase, which eases product separation and catalyst recovery. Along those same lines, it has been found that catalyst is not lost through leaching during the reaction.<sup>1</sup> Also, the structure of the organometallic catalytic species is maintained because there is no direct tethering or other change to the catalyst, which should allow the catalyst to maintain its properties as well. The problem of methane solubility is also avoided, or limited, because the reactions are found to occur

at the aqueous-organic interface, and the high surface area support results in a large amount of interfacial area.<sup>1</sup>

The SAP catalyst was first introduced by Mark Davis and co-workers in 1989, using a Rh SAP catalyst for liquid phase hydroformylation.<sup>3</sup> The catalytic species used was  $\text{HRh}(\text{CO})(\text{TPPTS})_3$ , where TPPTS is the trisodium salt of tri-(*m*-sulfonphenyl)-phosphine. The SAP catalyst was prepared by stirring an aqueous solution of the Rh complex and excess TPPTS ligand over degassed controlled-pore glass, CPG-240, followed by vacuum drying, yielding a free-flowing powder.<sup>1</sup> The catalyst was hydrated prior to use by allowing the catalyst to adsorb water vapor from a communicating vessel.<sup>1</sup> The SAP catalyst was characterized by FTIR, electron microprobe, NMR and TGA, to determine water content.

The SAP catalyst was tested for activity in the hydroformylation of oleyl alcohol. In a heterogeneous reaction with dehydrated SAP catalyst, they found 96.6% conversion to aldehydes in 5.5 hours, with no catalyst decomposition.<sup>1</sup> For comparison, a two-phase reaction was also carried out, with the substrate in organic solvent was reacted with an aqueous solution of unsupported Rh catalyst. In this case, no conversion to aldehyde was detected after 13 hours, and the catalyst decomposed.<sup>1</sup> Also, a heterogeneous reaction was carried out with solid, unsupported Rh catalyst, yielding 98.7% conversion to aldehydes after 5.2 hours.<sup>1</sup>

This study also investigated the influence of water content (Figure 2.3). Activity, regioselectivity and stability were all found to be dependent on the water content.<sup>1</sup> The plot of water dependence was interpreted as indicating 3 different environments. With low water content, the Rh complex adsorbs strongly to the surface, possibly decreasing

activity, and stabilizing the catalyst.<sup>1</sup> With intermediate water content, the maximum activity is found, while still maintaining catalyst stability.<sup>1</sup> With high water content, the catalyst loses both activity and stability, and approaches homogeneous behavior.<sup>1</sup> The increase in activity seems to be due to increased mobility, so at either extreme, the low water content seems to restrict motion and the high water content seems to bury the catalyst in water.

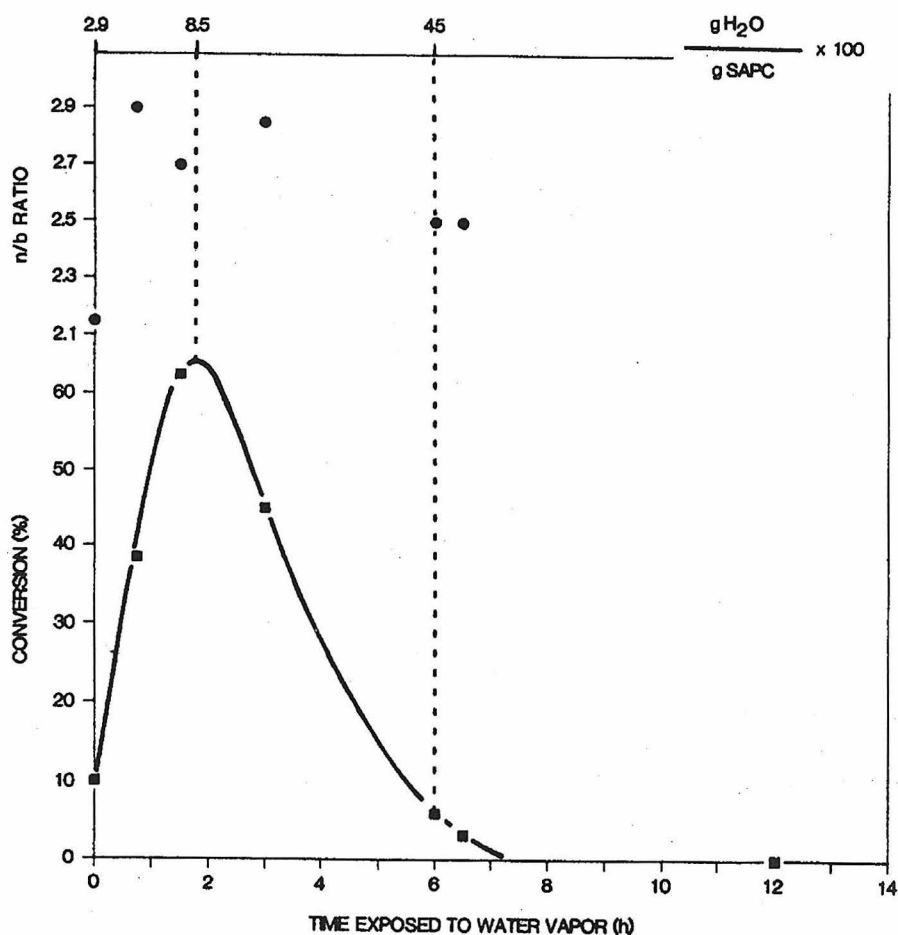


Figure 2.3.<sup>1</sup> Influence of SAP catalyst water content on conversion.

A supported-aqueous phase catalyst was also developed by Davis and co-workers for the Wacker oxidation system.<sup>4</sup> As well as avoiding the water insolubility of the substrates and easing product separation, further benefits for the Wacker chemistry include avoiding the corrosivity of  $\text{Cu}^{2+}$  co-catalyst by confining it to a support.<sup>4</sup> The

Pd/Cu SAP catalyst was prepared by stirring PdCl<sub>2</sub> over CPG-240 in ethanol, removing the solvent by rotary evaporation, stirring CuCl<sub>2</sub>•2H<sub>2</sub>O in H<sub>2</sub>O over the Pd-impregnated CPG, and removing the water by vacuum, yielding a free-flowing powder.<sup>4</sup>

The SAP catalyst activity was tested in the oxidation of 1-heptene. Oxidation to 2-heptanone was observed, along with significant isomerization of 1-heptene to 2- and 3-heptene.<sup>4</sup> It was found that more water was required to sufficiently hydrate the support and activate the catalyst than was needed for the Rh hydroformylation catalyst.<sup>4</sup> This is likely due to the relative affinity of the catalysts for water.<sup>4</sup> This Wacker system also showed an oxygen partial pressure dependence, suggesting that the reoxidation of Pd via the Cu<sup>2+</sup>/Cu<sup>+</sup>/O<sub>2</sub> couple may be slow.<sup>4</sup>

In reviewing these and other studies of SAP catalysts<sup>5-17</sup>, it becomes evident that every case is slightly different in terms of catalyst preparation, how the reaction is carried out, and the optimized conditions for reactivity. There are many variables that must be addressed.

The alkane oxidation study seemed to be a good candidate for SAP catalysis because of low substrate solubility and the importance of product separation and catalyst recyclability in this industrial valuable reaction. The aim of this part of my work is to take platinum complexes being investigated as catalysts for homogeneous methane oxidation, make them water soluble by sulfonating the ligand, support them on controlled-pore glass, and finally to test them for catalytic activity.

## EXPERIMENTAL METHODS

### General

The controlled-pore glass, CPG-240, was obtained from CPG, Inc., and used after washing with 1-L ultrapure water and drying overnight in 250°C oven. The potassium tetrachloroplatinate(II) was obtained from Pressure Chemical Co., and used as received.

### Catalyst Preparation

The Pt dimer was prepared by a modified version of a literature method.<sup>18</sup>

*cis/trans-Dichlorobis(dimethyl sulfide)Platinum(II)*. To a 500 mL, 3-necked, round-bottomed flask, outfitted with a magnetic stir bar, two rubber septa, and an Ar inlet with condenser, a solution of 7.0 g  $K_2PtCl_4$  in 100 mL DI water was added and stirred. To the solution, 9 mL dimethyl sulfide was added via syringe, producing a vomit-like pink/yellow mixture. The solution was heated with a heating mantle for approximately one hour, until the solution was bright yellow. Once the solution cooled to room temperature, it was extracted with five 50-mL portions of  $CH_2Cl_2$ , and the extracts were dried over anhydrous  $MgSO_4$  and filtered. The  $CH_2Cl_2$  was removed by rotary evaporation, and the product further dried on a vacuum line for approximately 45 minutes, yielding a bright yellow solid (4.93 g, 74.9%).

*Bis{Dimethy( $\mu$ -dimethyl sulfide)Platinum(II)}*. A 500-mL Schlenk tube, fitted with a magnetic stir bar and rubber septum, was charged with 3.9 g *cis/trans*- $[PtCl_2(SMe_2)_2]$ . The Schlenk tube and round-bottomed flask containing diethyl ether were backfilled with Ar three times. Using a cannula, approximately 160 mL dry diethyl ether was transferred to the Schlenk tube, which was then placed in an ice bath, with the ice level at least 3 cm above mixture level, and stirred for approximately 30 minutes. A

flask of a 1.4 M solution of MeLi in diethyl ether was backfilled with Ar three times, and 16 mL was extracted into a syringe, using a cannula, and was then added to the Schlenk tube drop-wise over 10 minutes. The solution was stirred for approximately 20 minutes, and a cold solution of 4.0 mL saturated  $\text{NH}_4\text{Cl}$  and 100 mL ice-cold DI water was added to the Schlenk tube. The solution was extracted with four 50-mL portions of ice-cold diethyl ether, using an ice-cold separatory funnel. The extracts were combined, dried over anhydrous  $\text{MgSO}_4$  in an ice-bath, and 0.2 g decolorizing charcoal was added for approximately five minutes. The solution was filtered into a 1-L round-bottomed flask, and the solvent was removed via rotary evaporation. The tannish powder was dried briefly on a vacuum line and stored in a freezer (2.15 g, 74.9%). The dimer was analyzed by  $^1\text{H}$  NMR.

The diimine ligand and Pt(II) and Pt(IV) diimine complexes were prepared following procedures outlined by Dr. Christoph Balzarek.

*Sulfonated diimine ligand.* To a 500-mL round-bottomed flask, outfitted with a magnetic stir bar, 10 g sulfonic acid sodium salt monohydrate was added, along with a spatula tip of sulfonic acid, and dissolved in approximately 250 mL fresh methanol. Using a syringe, 2 mL butanedione was added. The flask was fitted with a condenser and drying tube, and the solution was stirred overnight at approximately  $60^\circ\text{C}$ . After approximately 15 hours, significant precipitation had occurred. The slurry was cooled in an ice-bath, filtered with a Buchner funnel, and the product washed with 50 mL cold methanol. The tan solid was dried in vacuo (6.47 g, 64.4%).

*Sulfonated diimine dimethyl Platinum(II).* To a Schlenk tube, fitted with a magnetic stir bar and screw top, 1.005 g Pt dimer and 1.626 g diimine ligand were added.



The Schlenk tube and a round-bottomed flask of methanol were backfilled with Ar three times. Using a cannula, the Schlenk tube was filled approximately halfway with methanol, sealed and stirred, the tan mixture turning burgundy upon stirred at room temperature. The tube was immersed and 1/3 of the way in an oil bath, heating at 50°C overnight. The slurry was then cooled in an ice-bath and vacuum-filtered using a medium glass frit. The burgundy precipitate was rinsed with 50-mL ice-cold methanol and dried in vacuo for several hours (1.75 g, 75.4%). The compound was characterized by IR, UV/Vis,  $^1\text{H}$  NMR and  $^{13}\text{C}$  CP-MAS NMR.

*Sulfonated diimine dimethyl Platinum(IV)*. In a round-bottomed flask, 500 mg Pt(II) diimine complex was dissolved in 10 mL water. Upon the addition of 0.7 mL 30%  $\text{H}_2\text{O}_2$ , the solution began to bubble and the color faded to yellowish. The solution was stirred for about 30 minutes, until no more gas evolved. Then 100 mL THF was added, causing a brown oil to separate out. The THF/ $\text{H}_2\text{O}$  solution was decanted, and 25 mL acetone was added, causing a yellowish/tan solid to precipitate out. The acetone was decanted, and several small portions of acetone were added, swirled and decanted until all the water was removed. The tan solid was dried in vacuo (approximately 300 mg). The product was analyzed by IR and UV/Vis.

*Pt(II) diimine/CPG*. To a round-bottomed flask, 105 mg Pt(II) diimine and 2 g CPG were added, along with a stir bar, and the flask was backfilled with Ar three times. Using a cannula, approximately 15 mL degassed water was transferred into the flask, and the slurry was stirred for one hour. The water was then removed by vacuum, with stirring and gentle heating via warm water bath, leaving a free-flowing burgundy powder (approximately 5% Pt(II) diimine by weight). An approximately 20-weight percent

sample was also prepared in a similar manner. The samples were stored in a glove box. The supported compounds were analyzed by  $^{13}\text{C}$  CP-MAS NMR.

*Pt(IV) diimine/CPG.* To two separate round-bottomed flasks, each fitted a septum, 250 mg Pt(IV) diimine and 1 g CPG plus stir bar were added, respectively, and backfilled with Ar three times. Using a cannula approximately 10 mL degassed water was transferred into the flask containing the Pt(IV) and was swirled to dissolve. The Pt(IV) solution was transferred to the CPG flask, using a cannula, and the slurry was stirred for one hour. The water was removed by vacuum overnight, with stirring and gentle heating via warm water bath, leaving a free-flowing brown powder (approximately 20% Pt(IV) diimine by weight). The sample was stored in a glove box, and was characterized by  $^{13}\text{C}$  CP-MAS NMR.

### **Oxidation Study**

The behavior of supported Pt(II) diimine was investigated by comparing four samples, with approximately 20 weight percent loadings. The first sample was taken as made, straight out of the glove box. The second was exposed to air all day. The third and fourth were both hydrated by placing in a desiccator with a supersaturated solution of NaCl in water (relative humidity 75%). The third sample was hydrated overnight, placed in a round-bottomed flask, and exposed to pure  $\text{O}_2$  via balloon overnight. The fourth sample was held in the hydrating desiccator. The samples were analyzed by TGA and  $^{13}\text{C}$  CP-MAS NMR.

### **Analytical Methods**

Solution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian 300 MHz spectrometer, using  $\text{D}_2\text{O}$  as solvent. Solid state CP-MAS  $^{13}\text{C}$  NMR spectra were

recorded on Avance 200 MHz and 500 MHz spectrometers. The solid state NMR rotors were packed in a glove box. Thermogravimetric analyses (TGA) were performed in N<sub>2</sub> on a Netzsch STA449C Jupiter. Infrared spectra of samples in KBr pellets were obtained on a Nicolet Nexus 470 FT-IR. The UV/Vis spectra were obtained using a Varian Cary 3G UV-Visible Spectrophotometer.

## **RESULTS/DISCUSSION**

### **SAP Catalyst Solid State NMR Characterization**

The supported Pt diimine compounds were studied primarily by solid state <sup>13</sup>C CP-MAS NMR. The NMR spectrum of the supported Pt(II) sulfonated diimine, with an approximately 20 weight percent loading, was compared to that of the unsupported complex. While the spectrum of the supported complex was noisier, it is possible to identify all carbon peaks on both spectra. This indicates that the complex maintains its structure while supported. It is possible that, due to the high loading, clumps of Pt diimine have formed, rather than a supported aqueous layer of Pt diimine in solution. A sample with a 5 weight percent loading was also prepared and characterized by NMR, and again, all the carbon peaks were clearly identified in the spectrum. The NMR data suggests that the complex has been successfully supported, but at this point, it is impossible to state for certain the exact structure of the catalyst.

The unsupported Pt(II) sulfonated diimine was oxidized to a Pt(IV) sulfonated diimine, and this complex was also supported on controlled-pore glass, with an approximately 20 weight percent loading. Solid state NMR of this complex indicates that it is a different species than the supported Pt(II) complex. The most noticeable difference in the spectra

is the downfield shift of the Pt-methyl peak. In the Pt(II) spectrum, this peak lies around  $-12$  ppm, but in the Pt(IV) spectrum, this peak has shifted to  $-3$  ppm.

### **Oxidation Study**

The purpose of this study was to investigate the behavior of the supported Pt complexes, to determine whether the supported compound would react similarly to its unsupported counterpart. The specific reaction attempted was the relatively easy oxidation of Pt(II) to Pt(IV). The  $^{13}\text{C}$  CP-MAS NMR spectra of the sample exposed to air was unchanged when compared to the fresh, as-made sample, and TGA data revealed it had picked up some water from the air. The sample that had been hydrated overnight and exposed to pure  $\text{O}_2$  was also unchanged by NMR and had picked up about the same amount of water as the sample in air. The last sample, which was hydrated in air extensively by the supersaturated NaCl solution, underwent a color change from burgundy to brown. The NMR data suggests that this sample was actually oxidized to Pt(IV) – the Pt-methyl peak had shifted downfield to around  $-5$  ppm, similar to the spectrum of the prepared Pt(IV) diimine/CPG sample. The Pt(II) diimine was able to undergo oxidation to its Pt(IV) counterpart while being supported on controlled-pore glass. This sample had picked up the most water, but still only about 1% more water by weight. Perhaps it was the small difference in hydration that allowed the oxidation to take place, or it could have simply been the greater amount of time the oxidized sample had in which to undergo the oxidation.

## CONCLUSION

Supported aqueous phase catalysts have been used in a wide variety of reactions, and seem to remedy the downsides of solution chemistry, while maintaining the activities and selectivities that characterize homogeneous catalysis. Alkane oxidation is an industrially important reaction with potentially widespread benefits. With all that is known of SAP catalysts, it seems reasonable that a SAP system could be developed to carry out alkane oxidation. In my work, I was able to prepare water-soluble Pt compounds and to support them on controlled-pore glass. The supported compounds were detected by NMR, the spectra suggesting they were successfully supported, remaining structurally intact. Studies of the supported compounds indicated that they are able to undergo reactions similarly to unsupported compounds, as the Pt(II) diimine was oxidized to the Pt(IV) diimine while supported.

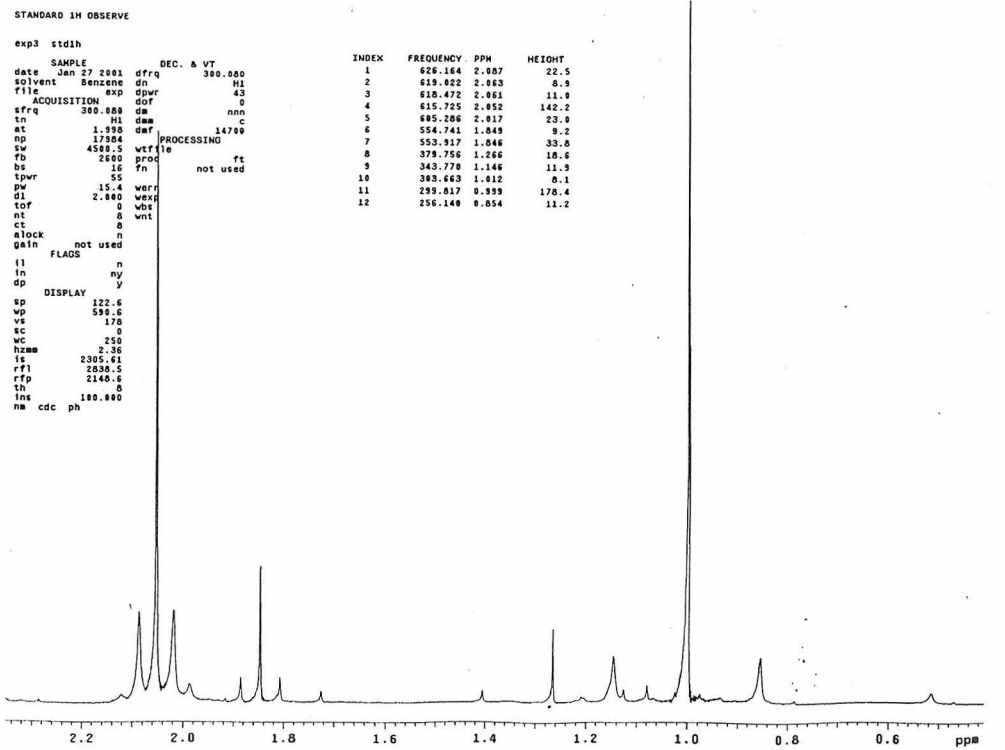
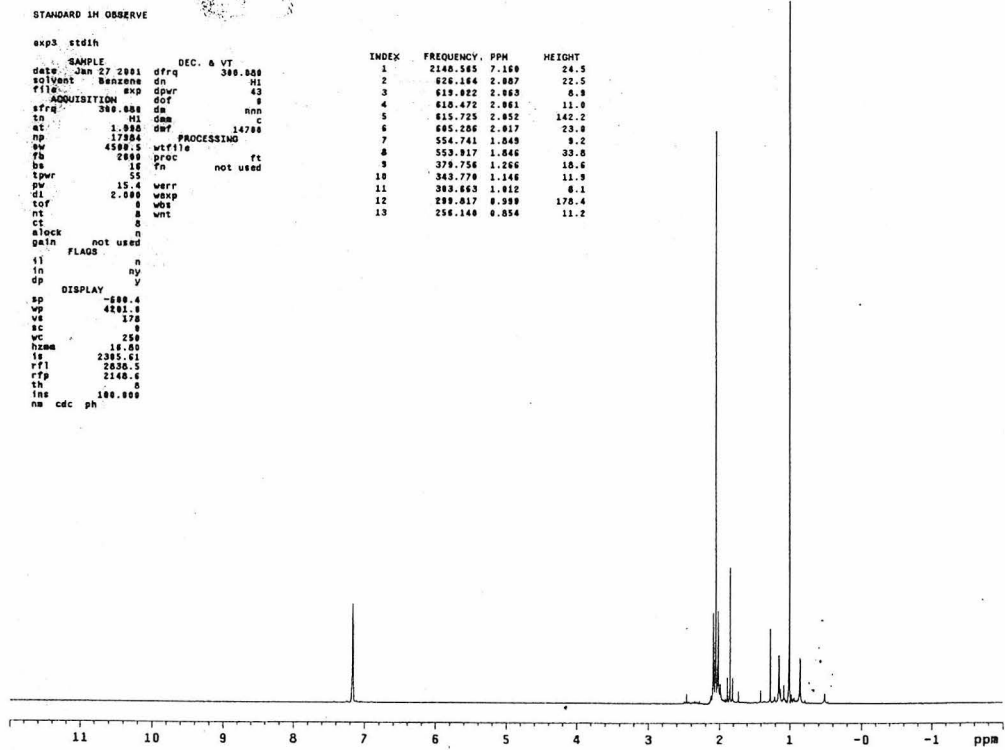
The main difficulty with this study was that outside of the Shilov system, there is no catalyst that is able to carry out the complete oxidation cycle. Furthermore, research into the water-soluble Pt compounds is still in the early stages. Therefore, there were no real reactions available in which to further test the reactivity of the supported complexes. When further developments are made in the homogeneous studies, it seems reasonable that a working SAP catalyst system could be developed.

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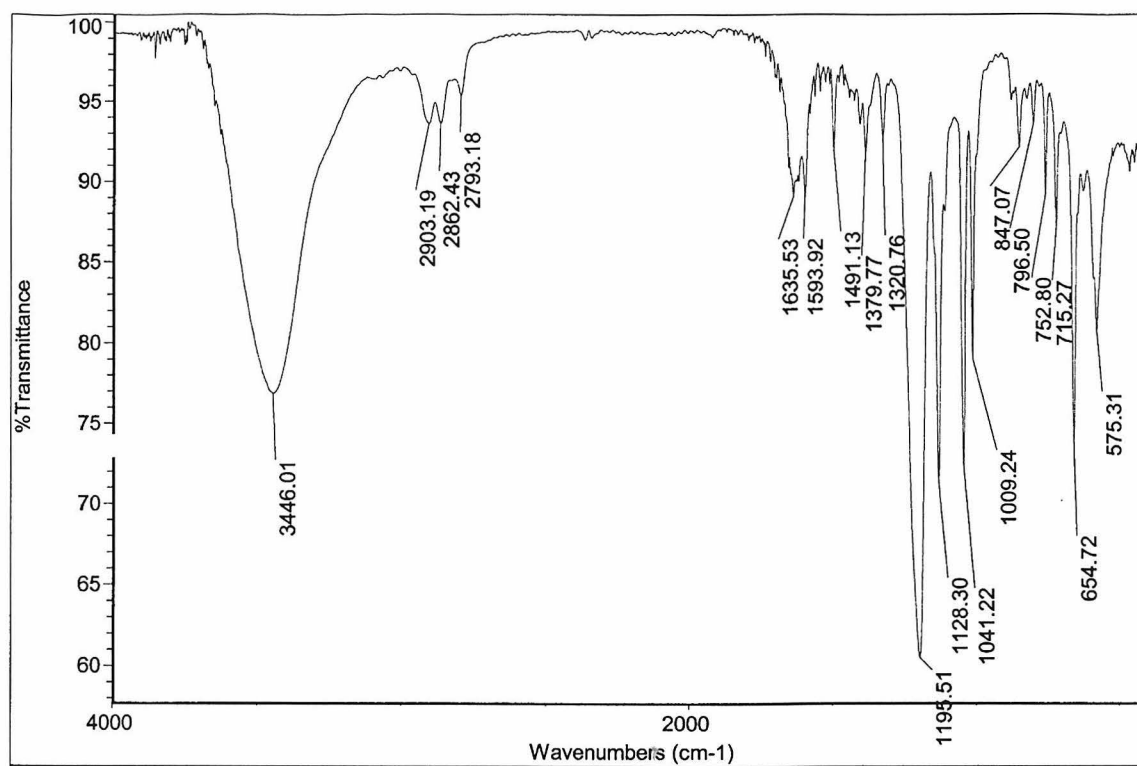
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SPECTRA

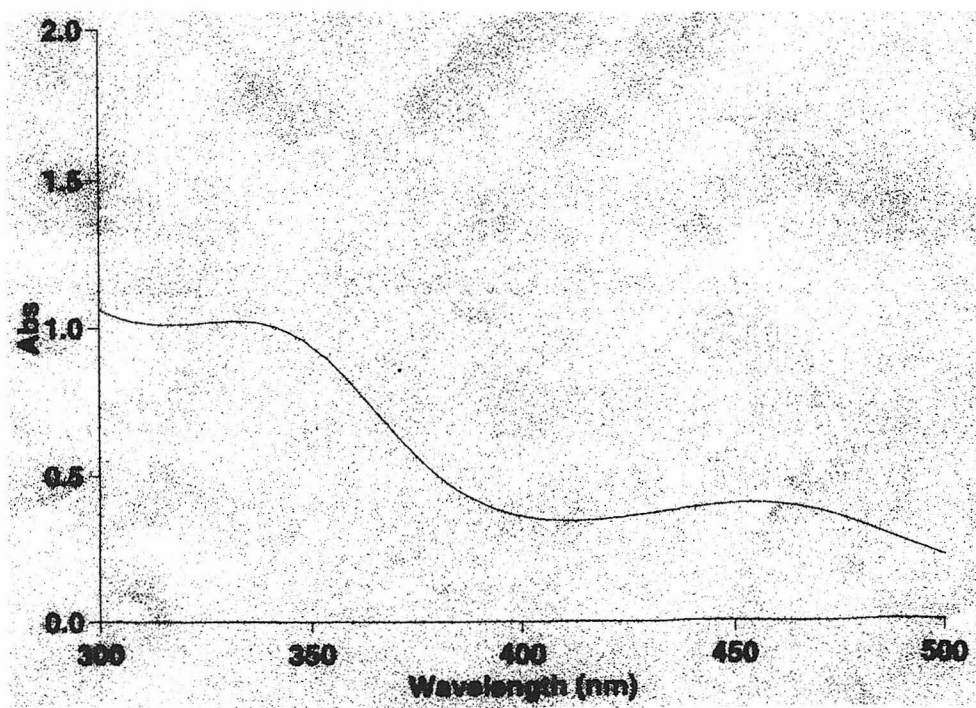
<sup>1</sup>H NMR spectra of Pt dimer



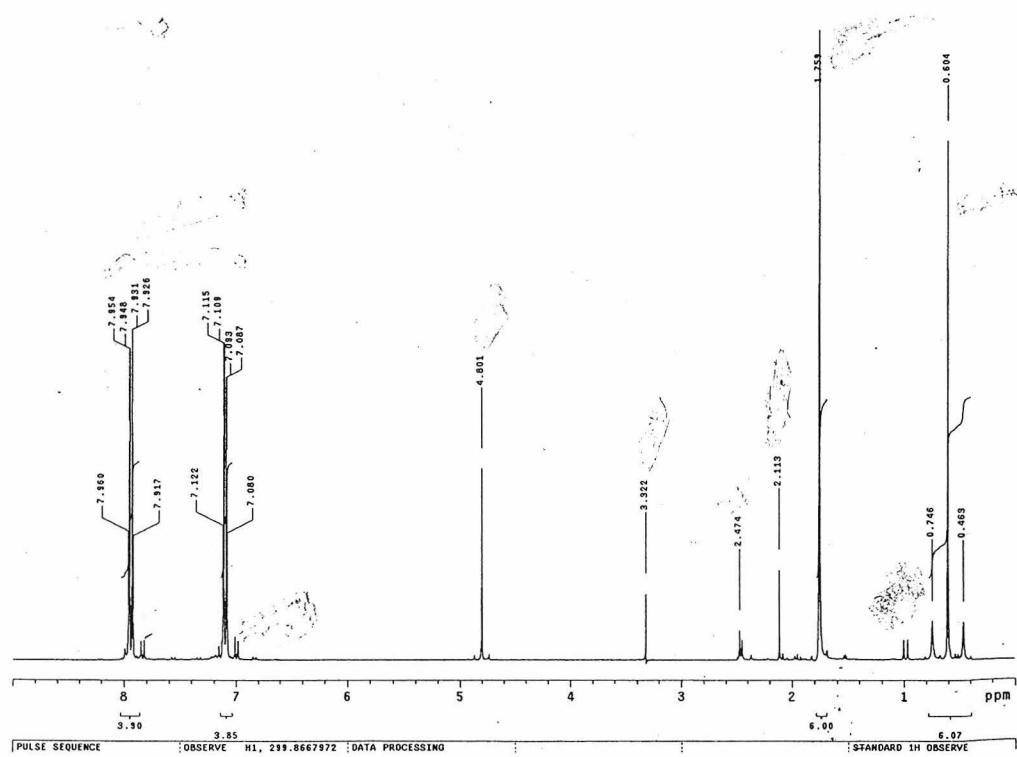
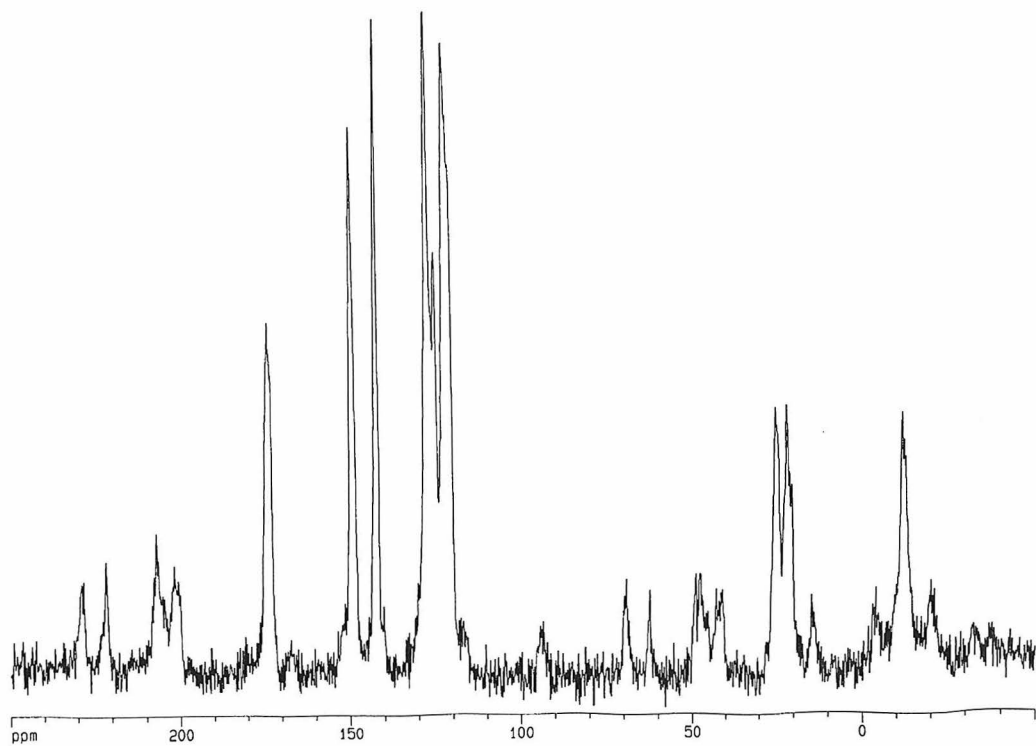
## IR of sulfonated Pt(II) diimine



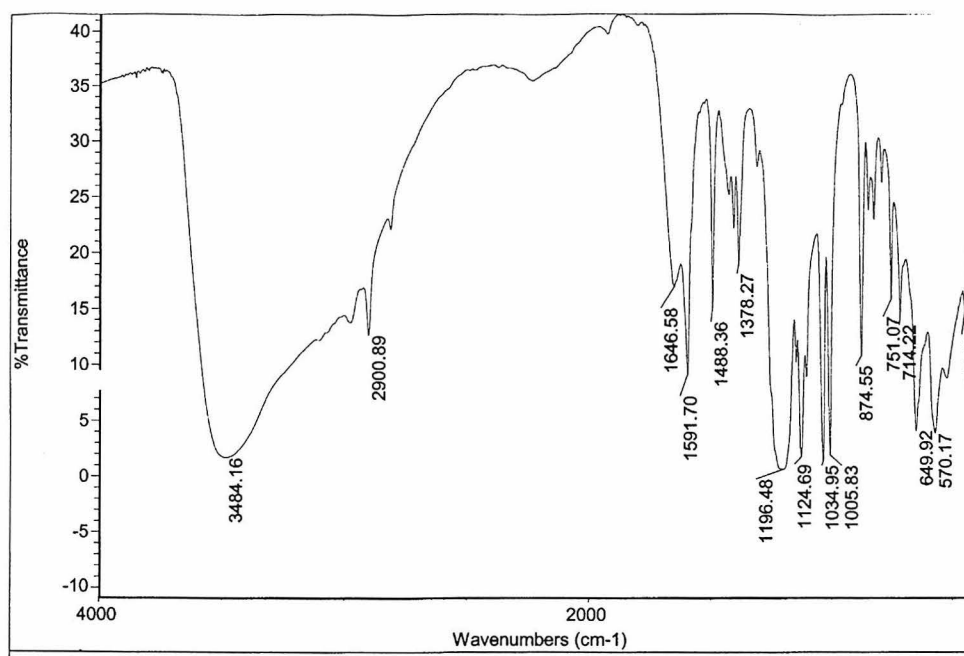
## UV/Vis of sulfonated Pt(II) diimine



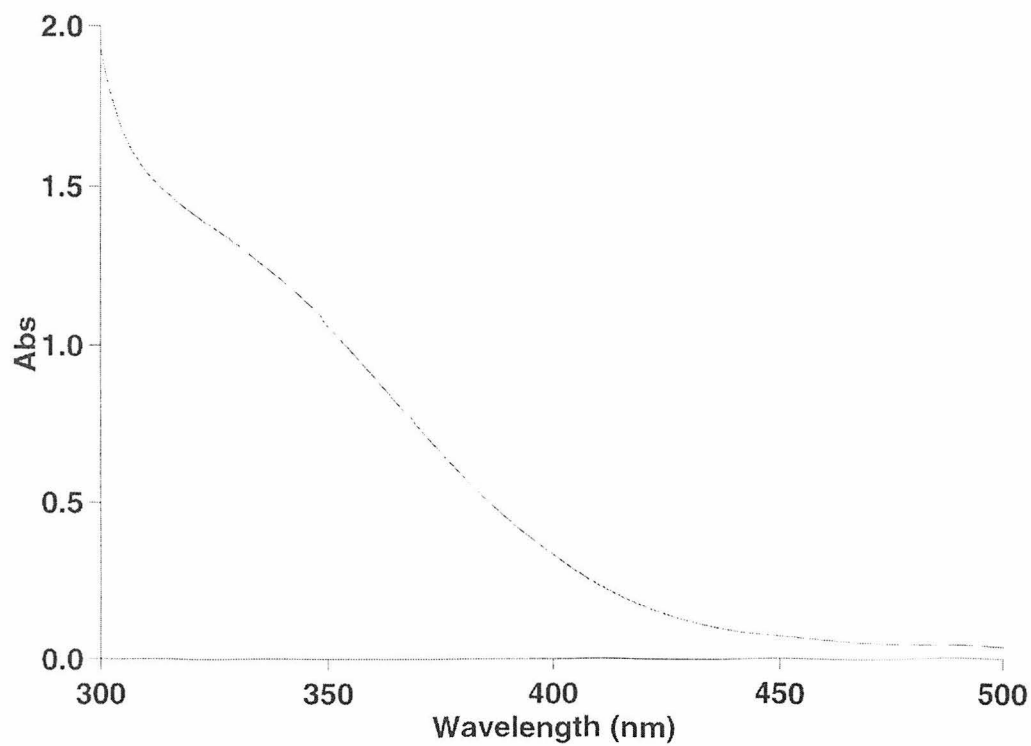


$^1\text{H}$  NMR spectrum of sulfonated Pt(II) diimine $^{13}\text{C}$  CP-MAS NMR spectrum of sulfonated Pt(II) diimine

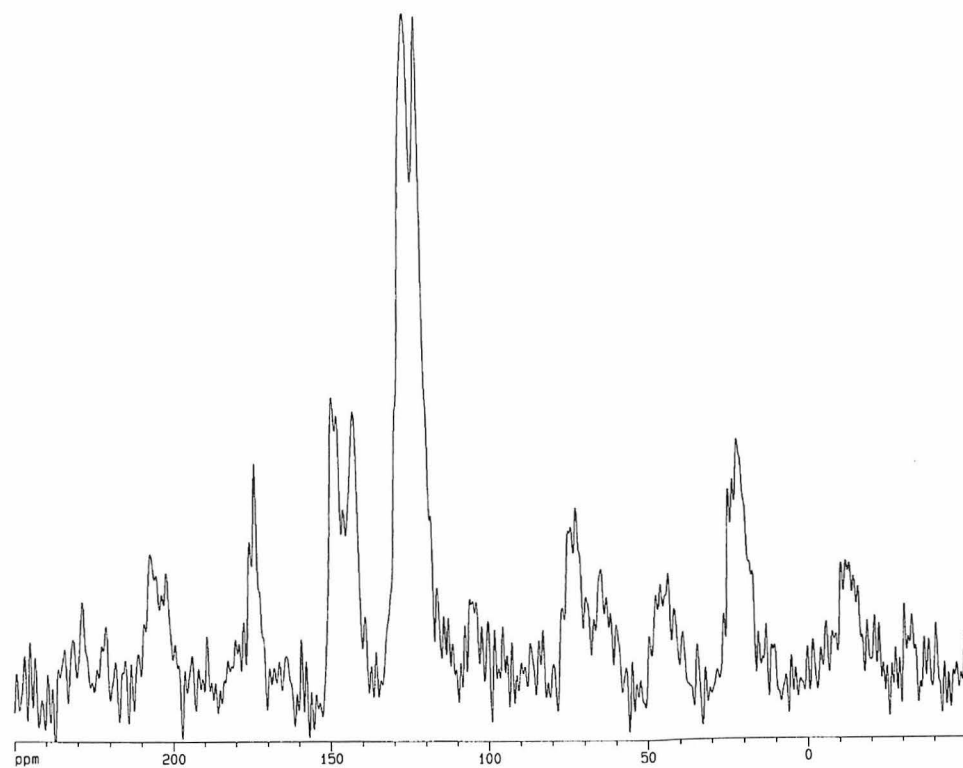
## IR of sulfonated Pt(IV) diimine



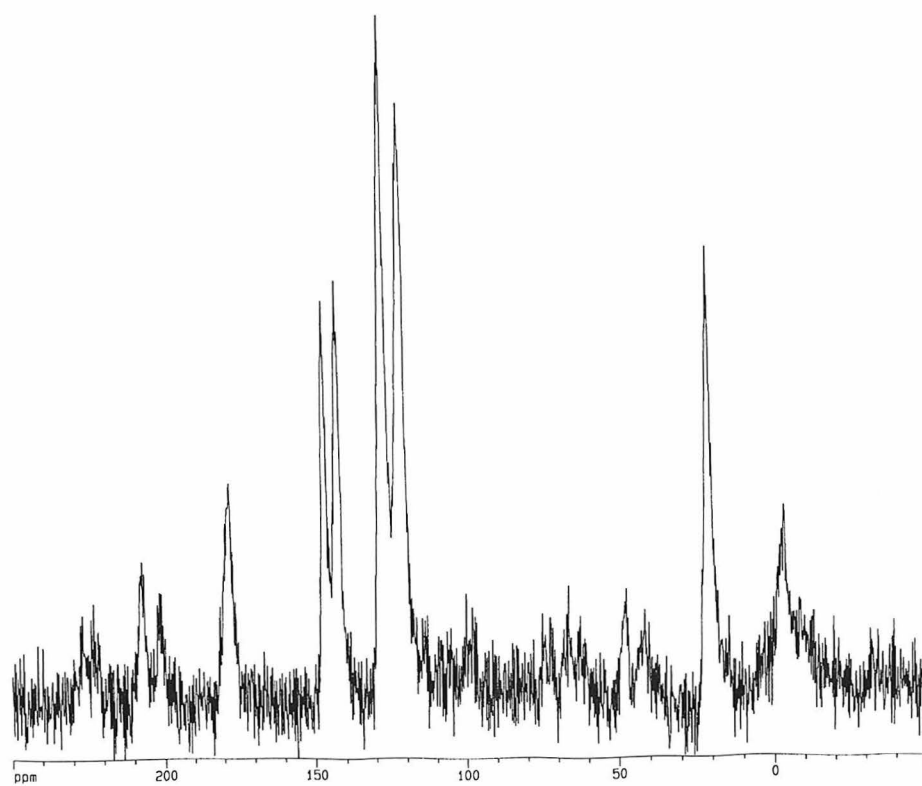
## UV/Vis of sulfonated Pt(IV) diimine



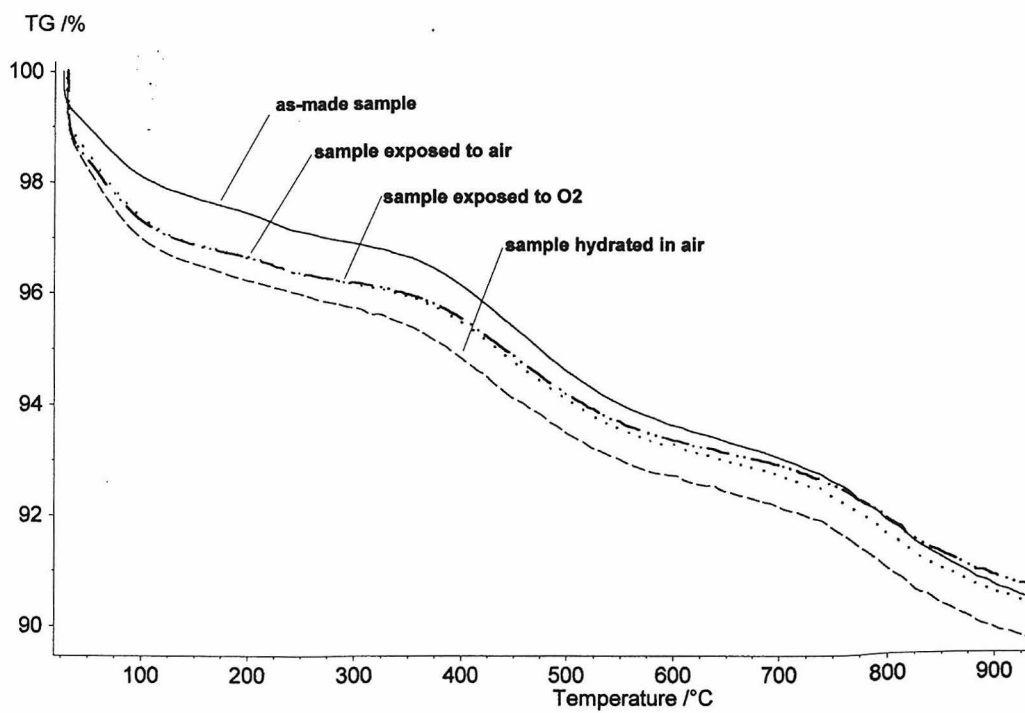
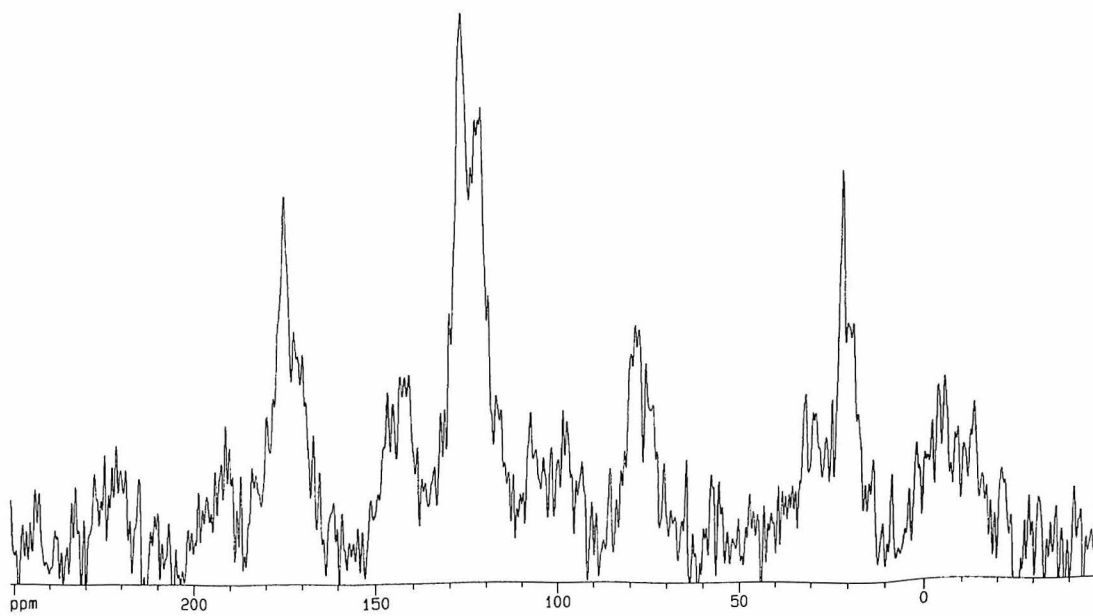
$^{13}\text{C}$  CP-MAS NMR spectrum of Pt(II) diimine/CPG



$^{13}\text{C}$  CP-MAS NMR spectrum of Pt(IV) diimine/CPG



## TGA comparison of as-made Pt(II)/CPG and hydrated Pt(II)/CPG

 $^{13}\text{C}$  CP-MAS NMR spectrum of Pt(II)/CPG hydrated in air

### 3. PLATINUM/COPPER CATALYST SYSTEM FOR ALKANE HYDROXYLATION

#### INTRODUCTION

Alkane conversion, particularly the partial oxidation to hydroxylated product, is a very important area of chemistry. It is the aim of a considerable amount of research due to its value as a longstanding chemical problem, but more importantly as an industrially valuable process, with far-reaching effects into as a fuel source and chemical feedstock. Work in the area of alkane hydroxylation has largely centered on the Shilov cycle, discussed in Chapter 2. Some research focuses on developing new organometallic catalysts to carry out this chemistry, hoping to make use of the wide range of possibilities and unique selectivities available with organometallic complexes.<sup>1</sup> Other studies have worked to replace the Pt(IV) oxidant with less expensive oxidants, especially O<sub>2</sub>.<sup>1,2</sup> This area of working with the oxidants is especially important because the major limitation to the Shilov system is the stoichiometric use of the prohibitively costly Pt(IV).

One promising possibility is the use of a Wacker-like Pt/Cu system. The Wacker reaction, shown in Equations (5) – (8), is a palladium/copper catalyzed partial oxidation of olefins to ketones or aldehydes, which uses molecular oxygen as the oxidant.<sup>3</sup> Several features of this system make it attractive for use with Shilov chemistry. First of all, the catalyst system is simply a mixture of metal salts, PdCl<sub>2</sub> and CuCl<sub>2</sub>•2H<sub>2</sub>O, which are similar to the salts used in the original Shilov cycle. These catalysts are water-soluble

and the reaction can be carried out in water.<sup>3</sup> Secondly, the palladium reoxidation in the Wacker cycle, Equations (6) and (7), is carried out by a  $\text{Cu}^{2+}/\text{Cu}^+/\text{O}_2$  couple, making dioxygen the stoichiometric oxidant.<sup>3</sup> Upon application to the Shilov cycle, this would constitute only a small modification to the Pt(II) oxidation step, as shown in the revised Shilov system in Figure 3.1. The oxidation via reduction from Pt(IV) to Pt(II) would now be done using the  $\text{Cu}^{2+}/\text{Cu}^+/\text{O}_2$  couple. A third attractive feature to the Wacker chemistry is that, as shown by Arhancet et al.<sup>3</sup>, this catalyst system is completely adaptable as a supported aqueous phase catalyst. Therefore, if a platinum/copper system were developed for alkane hydroxylation, using dioxygen as the oxidant, this system would likely work in the supported aqueous phase as well.

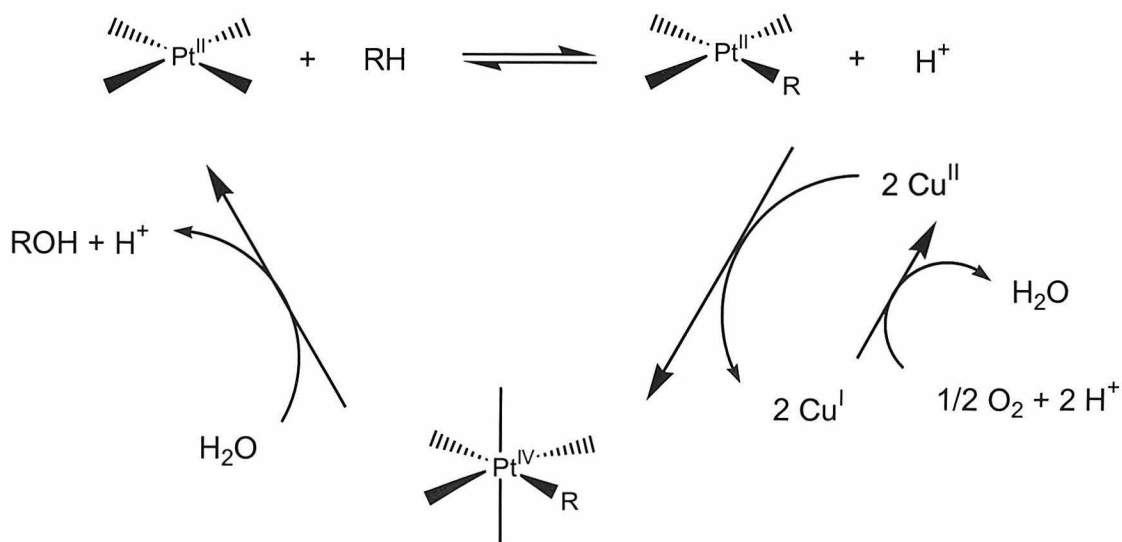
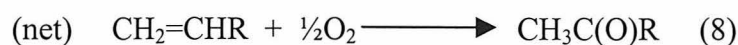
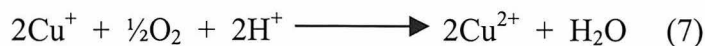


Figure 3.1. Revised Shilov cycle alkane hydroxylation using dioxygen as the oxidant.

Some work has been done using homogeneous platinum/copper catalyst systems for alkane hydroxylation. Sen and coworkers<sup>4</sup> have reported the catalytic oxidation of ethanesulfonate using Pt(II)/Cu(II) and Pt(IV)/Cu(II) systems. They find that with the proper cocatalyst at elevated temperature, Shilov chemistry can be catalytic with dioxygen as the ultimate oxidant.<sup>4</sup> Mechanistic studies indicate that, for the most part, the C-H activation occurs by the same pathway as with the Shilov system.<sup>4</sup>

Extensive studies into the catalytic oxidation of ethanesulfonate were reported (Table 3.1).<sup>4</sup> The reaction was carried out in water, and sulfuric acid was added to give low pH.<sup>4</sup> They used an oxygen partial pressure of 300 psi, reaction temperature was 160° C, and the reaction was carried out for four hours.<sup>4</sup> They reported only a modest effect on reaction rate with increasing oxygen pressure.<sup>4</sup> The primary reaction was observed to be the hydroxylation of the remote methyl group.<sup>4</sup> It was found that in the absence of oxygen, K<sub>2</sub>PtCl<sub>4</sub>, both alone and with one equivalent of CuCl<sub>2</sub>, allowed for one turnover to HOCH<sub>2</sub>CH<sub>2</sub>SO<sup>3-</sup>, sulfonated ethanol.<sup>4</sup> They also observed the precipitation of platinum metal.<sup>4</sup> The results of primary importance to the study at hand are those found using the K<sub>2</sub>PtCl<sub>4</sub>/CuCl<sub>2</sub> and Na<sub>2</sub>PtCl<sub>6</sub>/CuCl<sub>2</sub> catalyst systems, which produced the highest number of turnovers per Pt. With the Pt(II)/Cu(II) system, the Cu:Pt mole ratio was 6, while in the Pt(IV)/Cu(II) system it was 8.

Besides ethanesulfonate, Sen and coworkers also carried out the catalytic hydroxylation of several other substrates, using Pt(IV) with a Cu(II) cocatalyst. The results from these experiments are summarized in Table 3.2.<sup>4</sup> In each case, the major product was that formed by the hydroxylation of the strongest C-H bond of the substrate.<sup>4</sup>

catalyst (mmol)	HOCH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> <sup>-</sup> (mmol)	(HO) <sub>2</sub> CHCH <sub>2</sub> SO <sub>3</sub> <sup>-</sup> (mmol)	HO <sub>2</sub> CCH <sub>2</sub> SO <sub>3</sub> <sup>-</sup> (mmol)	HOCH <sub>2</sub> CO <sub>2</sub> H (mmol)	CH <sub>3</sub> CO <sub>2</sub> H (mmol)	turnovers/ Pt
K <sub>2</sub> PtCl <sub>4</sub> (0.012)	0.02	0.01	0	0	0	2
K <sub>2</sub> PtCl <sub>4</sub> (0.015) NaCl (0.15)	0.12	0.02	0	0.02	0.01	11
K <sub>2</sub> PtCl <sub>4</sub> (0.015) NaCl (0.30)	0.03	0.01	0	tr.	tr.	3
K <sub>2</sub> PtCl <sub>4</sub> (0.012) CuCl <sub>2</sub> (0.074)	0.50	0.12	tr.	0.01	0.01	43
Na <sub>2</sub> PtCl <sub>6</sub> (0.009)	0.04	0.02	0	0	0	7
Na <sub>2</sub> PtCl <sub>6</sub> (0.009) CuCl <sub>2</sub> (0.074)	0.24	0.08	0.06	0.08	0.01	52
Pt metal (0.014) CuCl <sub>2</sub> (0.074)	0.02	0.05	0.02	0.01	0.02	9
Pt metal (0.014) CuSO <sub>4</sub> (0.074)	0	0	0	0	0	0
CuCl <sub>2</sub> (0.074)	0	0	0	0	0	0

<sup>a</sup> Reaction conditions: C<sub>2</sub>H<sub>5</sub>SO<sub>3</sub>Na, 2.0 mmol; H<sub>2</sub>O, 2.0 mL; H<sub>2</sub>SO<sub>4</sub>, 0.1 mL; O<sub>2</sub>, 300 psi; N<sub>2</sub>, 1200 psi; 160 °C; 4 h.

Figure 3.1.<sup>4</sup> Catalytic oxidation of ethanesulfonate.



They reported that methanesulfonate was the slowest reacting substrate and suggested that the close proximity of the electron-withdrawing sulfonate group makes the adjacent C-H bond less susceptible to electrophilic attack.<sup>4</sup> Further, with the methanesulfonate substrate, only 8 turnovers/Pt were observed.<sup>4</sup> Interestingly, the catalyst system used in this reaction had an unexplained low Cu:Pt mole ratio, only 3.6 compared to 10 in the ethanesulfonate reaction. Perhaps the low turnover number is due to the lower amount of copper.

Na <sub>2</sub> PtCl <sub>6</sub> (mmol)	substrate	$\omega$ -hydroxy (mmol)	( $\omega-1$ )-hydroxy (mmol)	turnover/ Pt
0.028	CH <sub>3</sub> SO <sub>3</sub> Na	0.23	N/A	8
0.010	C <sub>2</sub> H <sub>5</sub> SO <sub>3</sub> Na	0.53	0	53
0.005	C <sub>3</sub> H <sub>7</sub> SO <sub>3</sub> Na	0.15	0.03	28
0.005	C <sub>2</sub> H <sub>5</sub> PO <sub>3</sub> H	0.17	0	35
0.010	C <sub>2</sub> H <sub>5</sub> COOH	0.16	0	16

<sup>a</sup> Reaction conditions: substrate, 2.0 mmol; CuCl<sub>2</sub>, 0.1 mmol; H<sub>2</sub>O, 2 mL; H<sub>2</sub>SO<sub>4</sub>, 0.08 mL; O<sub>2</sub>, 1300 psi; 150 °C, 4 h.

Table 3.2.<sup>4</sup> Catalytic hydroxylation of organic acid substrates.

Sen and coworkers also carried out direct competition reactions between ethane and ethanesulfonate to compare their relative reactivities (Table 3.3).<sup>4</sup> According to their calculations, the amount of hydroxylated product formed from ethane was equal to or greater the amount from ethanesulfonate.<sup>4</sup> In comparing the reactivity with both Pt(II)/Cu(II) and Pt(II)/Pt(IV) catalysts, they find no change in relative reactivities, indicating that the copper ion is not involved in the C-H activation.<sup>4</sup> Interestingly, in these reactions, they utilize Cu(II):Pt(II) and Pt(IV):Pt(II) mole ratios of only 1.5. Also, the ethane reacts to form more products than they report for ethanesulfonate, and the

catalyst (mmol)	$C_2H_5SO_3^-$ (mmol) <sup>d</sup>	product (mmol)	$C_2H_5SO_3^-$ consumed/Pt	$C_2H_6$ (mmol) <sup>e</sup>	products (mmol)	$C_2H_6$ consumed/Pt
$PtCl_4^{2-}$ (0.024)	0.124	$HOOC_2H_4SO_3^-$ (0.062)	2.6	0.062	$C_2H_5OH$ (0.021) $HOOC_2H_4OH$ (0.028) $CH_3CO_2H$ (0.012)	2.5
$PtCl_4^{2-}$ (0.024) $PtCl_6^{2-}$ (0.036) <sup>f</sup>	0.124	$HOOC_2H_4SO_3^-$ (0.027)	0.6	0.062	$C_2H_5OH$ (0.011) $HOOC_2H_4OH$ (0.011) $CH_3CO_2H$ (0.005)	0.6

<sup>a</sup> Reaction conditions:  $H_2O$ , 2 mL;  $C_2H_6$ , 550 psi;  $O_2$ , 200 psi; 160 °C, 4 h. <sup>b</sup> 0.03 mL of  $H_2SO_4$  was added. <sup>c</sup> 0.03 mL of HCl was added.

<sup>d</sup> Initial amount. <sup>e</sup> Calculated for 100 °C from data in International Critical Tables; the number should be lower for 160 °C. Amount present in solution does not change with time because of the presence of ethane in the headspace.

Table 3.3.<sup>4</sup> Relative reactivity of ethanesulfonate and ethane.

singly hydroxylated product is no longer the major product, but is nearly equivalent with the doubly hydroxylated product.<sup>4</sup>

Tom Baker and Geoffrey Brown carried out work at Los Alamos National Labs, which was done in collaboration with the methane conversion project at Caltech. They attempted to reproduce Sen's work using quartz tubes in a high-pressure reactor. They were looking, in particular, to identify the effect  $\text{CuCl}_2$  had on the Pt-catalyzed oxidation of ethanesulfonate with dioxygen. They carried out their reactions using 300 psi  $\text{O}_2$ , with a reaction temperature of  $160^\circ\text{C}$ , and reaction times of both 4 and 12 hours. Overall, they did observe general reproduction of Sen's findings. However, they did not find the addition of sulfuric acid to be necessary. In fact, when sulfuric acid was used, they found lower conversion and the formation of a small amount of platinum metal. In comparing 4- and 12-hour reactions, similar conversions were observed, indicating the catalyst is dead in less than 4 hours. Through their studies, they found that the addition of copper definitely inhibits platinum metal formation, which allows the platinum catalyst to last longer. With a Pt-only catalyst, there is clearly a mixture of homogeneous and heterogeneous catalysis, resulting in the formation of comparable amounts of acetic acid and hydroxyacetic acid. Only a trace of acetic acid is found in the Pt-Cu catalyst runs.

The work by Sen and coworkers and those at Los Alamos has some important implications for the methane conversion project, and provides an interesting jumping off point for further work in this field. The oxidation of ethanesulfonate shows that the Pt/Cu system does yield enough turnovers to identify and even quantify the products. Also, the relative reactivity study demonstrates that gas phase substrates can also be catalytically oxidized with this aqueous catalyst system. Very little work appears to have been done in

the area of methanesulfonate and nothing is reported regarding methane, which is the primary focus of this project. Therefore, the aim of this part of my work was to reproduce the work by Sen and Baker in my reactor system and to expand the work to include investigations of C1 alkanes – methanesulfonate and methane. Additionally, I began to work to develop supported aqueous phase Pt/Cu catalysts to test for activity towards alkane hydroxylation.

## **EXPERIMENTAL METHODS**

### **General**

The potassium tetrachloroplatinate(II) was obtained from Pressure Chemical Co., and used as received. The copper(II)chloride dihydrate was used as received from EM Science. The sodium hexachloroplatinate(IV) and sulfonated alkanes were obtained from Aldrich and used as received. The controlled-pore glass, CPG-240, was obtained from CPG, Inc., and used after washing with 1-L ultrapure water and drying overnight in 250° C oven.

### **Reactivity Studies**

The initial aim of these studies was to reproduce work done by Sen and coworkers<sup>4</sup>, so much of the experimental methods was taken from the procedures discussed in their study. The alkane hydroxylation reactions were carried out in a 25-mL, stainless steel Parr 4592 Micro Reactor with a Parr 4843 Temperature Controller, PID, with Ramp and Soak Programming. The reactor has a maximum pressure of 3000 psi, and utilizes a rupture disk good to 2000 psi. The reactor is outfitted with a pressure

gauge, two gas inlets, and a pressure relief valve. A glass liner with an approximately 20 mL volume was used for all reactions.

Throughout these studies, the reactor and especially the stainless steel thermocouple sheath were undergoing corrosion from the reaction mixtures. The reactor developed small pits in the inner walls and on the lid. The holes in the top and the thermocouple sheath appeared rusty after each reaction. Efforts were made to clean everything as well as possible between each reaction, but eventually the thermocouple sheath would crack, likely where the gas-liquid interface was during the reactions, and it would have to be replaced.

The reaction temperature program used for all reactions was a ramp from room temperature to 160° C in 30-45 minutes, followed by a 4-hour soak at 150-160 °C. An aqueous solution of catalyst and water-soluble substrate was loaded into the reactor in the glass liner. The reactor was then pressurized with O<sub>2</sub>, and alkane where specified. Following the reaction, the reactor was allowed to cool to room temperature and the pressure was released through the relief valve. Where specified, GC/MS was used to analyze the exhaust gas following a reaction. Product detection was done using <sup>1</sup>H NMR and GC/MS of the reaction solution.

The reactivity studies can be divided into four main sets of reactions by substrate: ethanesulfonate; ethane and ethanesulfonate; methanesulfonate; and methane, with and without methanesulfonate. The specifics of each set will now be discussed in further detail.

*Ethanesulfonate Reactions.* In the ethanesulfonate reactions, 2 mmol of the CH<sub>3</sub>CH<sub>2</sub>SO<sub>3</sub>Na substrate were dissolved in ultrapure water, along with the catalyst.

Approximately 0.015 mmol platinum catalyst, either  $\text{K}_2\text{PtCl}_4$ , Pt(II), or  $\text{Na}_2\text{PtCl}_6$ , Pt(IV), were used with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , at a Cu:Pt mole ratio of 6-9. Oxygen pressures of 300 and 925 psi were used, and reactions were also carried out in  $\text{D}_2\text{O}$ .

*Ethane and Ethanesulfonate Reactions.* The addition of ethane to the reaction complicated matters considerably. Attempts to replicate the pressures used by Sen and coworkers<sup>4</sup> resulted in huge pressure jumps, causing the rupture disk to burst on more than one occasion. By experimenting with various pressures, maintaining the  $\text{C}_2\text{H}_6:\text{O}_2$  ratio used by Sen, partial pressures of 440 psi  $\text{C}_2\text{H}_6$  and 160 psi  $\text{O}_2$  were chosen. For this set of reactions, 0.1-0.125 mmol ethanesulfonate were used in ultra-pure  $\text{H}_2\text{O}$ , and the catalyst was 0.025 mmol  $\text{K}_2\text{PtCl}_4$ , and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  at a Cu:Pt mole ratio of 9. An ethane-only reaction with a Cu:Pt mole ratio of 8 was also carried out.

*Methanesulfonate Reactions.* This reaction set is fairly similar to the ethanesulfonate reactions, but in Sen's work, the methanesulfonate reaction was carried out under slightly different conditions. So this set includes the reproduction of his work, as well as modifications to allow better comparison to the ethanesulfonate reactions. Again, 2 mmol of substrate,  $\text{CH}_3\text{SO}_3\text{Na}$ , were used in ultrapure  $\text{H}_2\text{O}$ . Approximately 0.028 mmoles of  $\text{K}_2\text{PtCl}_4$  or  $\text{Na}_2\text{PtCl}_6$  was used, with Cu:Pt mole ratios of 3.5 and 9. Oxygen pressures of 225 and 900 psi were used.

*Methane Reactions.* These reactions were carried out with Pt(II)/Cu(II) catalyst, using 0.025-0.028 mmol  $\text{K}_2\text{PtCl}_4$ , and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  at a Cu:Pt mole ratio of 8-10. Similarly to the ethane/oxygen reactions, partial pressures of 400 psi  $\text{CH}_4$  and 150 psi  $\text{O}_2$  were used. In the methane/methanesulfonate reactions, approximately 0.14 mmol  $\text{CH}_3\text{SO}_3\text{Na}$  were used. Reactions were carried out in both ultrapure  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ .

### Preparation of Supported Pt/Cu Compounds

The supported Pt/Cu compounds were prepared following the methods described for the Wacker oxidation Pd/Cu SAP catalyst.<sup>3</sup> The salts were supported on controlled-pore glass and were made with platinum alone, copper alone and platinum and copper, with a Cu:Pt mole ratio between 8 and 10. The compounds were prepared with 5 weight percent salt loadings and 5 weight percent metal loadings, which corresponds to an 11 weight percent salt loading. For the single salt samples,  $K_2PtCl_4$  or  $CuCl_2 \cdot 2H_2O$  was dissolved in ultrapure water and the resulting solution was stirred over the controlled-pore glass for 2-3 hours. The water was removed by rotary evaporation. For the Pt/Cu samples, the Pt salt was supported first, as described above, followed by a second impregnation with the Cu salt solution. Approximately 2 grams were prepared at a time, using about 10 mL of water for each impregnation. Thermogravimetric analyses were used to determine the water content of the resulting compounds.

### Analytical Methods

Solution  $^1H$  NMR spectra were recorded on a Varian 300 MHz spectrometer, using  $D_2O$  as solvent. The NMR spectra discussed are contained in the Spectra section. No internal standard was used, so analyses are qualitative only. Conversions were calculated as moles of products divided by the sum of the moles of product and moles of starting material. The mole values were determined by dividing the integration value by the number of hydrogens it represented. Occasionally the water peak, at 4.8 ppm, is so large that it partially buries the peaks near it, causing error in the integration values. The presence of paramagnetic copper in the solution could also account for the poor baselines. An Agilent Technologies 6890N Network GC System and 5973 Network Mass Selective

Detector, paired together, were used to obtain gas chromatography and mass spectroscopy data. Again, no internal standard or calibrations were used, so data is qualitative only. Gas samples were injected directly from the reactor's relief valve into the gas-sampling valve of the GC. Liquid samples were injected manually with a gas-tight syringe. In all cases, except for the methane reactions, the GC/MS analysis was done up to several months after the reaction took place, so changes in the solution could very well have occurred, indicating the presence of compounds not seen by NMR. Thermogravimetric analyses (TGA) of the Pt/Cu SAP compounds were performed in N<sub>2</sub> on a Netzsch STA449C Jupiter.

## RESULTS/DISCUSSION

### Reactivity Studies

*Ethanesulfonate Reactions.* The primary product observed in this set of reactions was HOCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub><sup>-</sup>, sulfonated ethanol. In the basic reaction with 300 psi O<sub>2</sub> and a Cu(II):Pt(II) mole ratio of 8, a conversion of 61%, corresponding to 102 turnovers/platinum was observed. The NMR spectrum clearly shows the starting material, the sulfonated ethanol product. A GC/MS of the product solution reported the presence of acetic acid and acetaldehyde, which likely correspond to the two smaller peaks, at about 2.1 and 1.72 ppm, respectively. This same reaction was repeated in D<sub>2</sub>O, with a Cu:Pt mole ratio of about 6. Again the starting material and hydroxylated product can be seen in the NMR spectrum. The conversion is slightly lower at 27%, with 30 turnovers/platinum. The lower conversion is likely due to the lower amount of copper. Acetic acid and acetaldehyde and now acetone were observed by GC/MS. The peak at



2.2 ppm in the NMR spectrum could be from acetone. The peaks just downfield from 2 ppm are broader than in the previous reaction, probably due to deuterium exchange. The reaction was repeated, again in D<sub>2</sub>O, with 925 psi O<sub>2</sub>. The results were very similar to the previous reaction but with a slightly higher conversion – 46%, with 68 turnovers/platinum. Ethanesulfonate conversion by Pt(IV)/Cu(II) was also tested, using 915 psi O<sub>2</sub> and a Cu:Pt mole ratio near 9. Due to the excess of chloride ion with the use of Na<sub>2</sub>PtCl<sub>6</sub>, the NMR spectra revealed the formation of both hydroxylated and chlorinated ethanesulfonate. The total conversion was calculated to be 32%, with 56 turnovers/platinum. No other products were detected by NMR or GC/MS.

*Ethane and Ethanesulfonate Reactions.* Through the work to find an appropriate pressure at which to run the reactions, it was observed that with low partial pressures, 150 psi C<sub>2</sub>H<sub>6</sub> and 55 psi O<sub>2</sub>, and 2 mmol ethanesulfonate substrate, the results were the same as the previous reactions, with no products from ethane observed. With partial pressures of 380 psi C<sub>2</sub>H<sub>6</sub> and 145 psi O<sub>2</sub>, the NMR showed the starting material, sulfonated ethanol, and peaks that could be due to ethanol – a triplet at 1.15 ppm and what appears to be a quartet at 3.6 ppm. The GC/MS confirmed the presence of ethanol. The GC/MS also detected acetic acid, which wasn't seen by NMR. In a reaction with slightly higher partial pressures, 440 psi C<sub>2</sub>H<sub>6</sub> and 175 psi O<sub>2</sub>, and a smaller amount of ethanesulfonate substrate, ethanol was generated again, indicated by both NMR and GC/MS. A few smaller peaks had grown into the NMR spectrum – ~1.3, 2.2, and 3.35 ppm. The presence of acetic acid was detected by GC/MS. This last reaction was repeated as ethane-only, without the addition of ethanesulfonate, and again ethanol was seen by both NMR and GC/MS. The peaks at 1.3 and 3.35 ppm were still present, but now the peak at

2.2 ppm, and a new one at 2.3 ppm, were dominating the spectrum. The GC/MS analysis indicated the presence of acetic acid and acetone, which could be responsible for the large peaks in the NMR.

*Methanesulfonate Reactions.* The reaction of methanesulfonate is a very straightforward conversion to  $\text{HOCH}_2\text{SO}_3^-$ . Reactions with 900 psi  $\text{O}_2$  and  $\text{Cu(II):Pt(II)}$  mole ratios near 9, resulted in approximately 30% conversion to product, with about 20 turnovers/platinum. These results are about half the maximum conversion found with ethanesulfonate substrate. With only 225 psi  $\text{O}_2$ , 22% conversion was obtained, with 15 turnovers/platinum. Lowering the mole ratio to 3.5, resulted in a very slight decrease in conversion to 27%, with 17 turnovers/platinum. Upon replacing  $\text{Pt(II)}$  with  $\text{Pt(IV)}$  and maintaining the 3.5 mole ratio, the conversion was lowered dramatically to 10.5%, with only 7 turnovers/platinum. This result is very close to that reported by Sen.<sup>4</sup>

*Methane Reactions.* The methane/methanesulfonate reaction was carried out in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The sulfonated methanol product is observed, as with the previous reaction set, and according to both NMR and GC/MS, methanol is also produced in these reactions. A GC/MS of the exhaust from the reaction in  $\text{H}_2\text{O}$  indicated the formation of chloromethane as well. The NMR of the  $\text{D}_2\text{O}$  reaction contained a very large peak at 2.2 ppm, while the spectrum of the  $\text{H}_2\text{O}$  reaction did not. But the GC/MS spectra from both reactions indicated the presence of acetic acid, as well as formic acid in the  $\text{D}_2\text{O}$  reaction. The methane-only reaction was also carried out in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The NMR spectra contain only a singlet at 3.33 ppm, which corresponds to methanol. Analysis of the exhaust gas in the  $\text{H}_2\text{O}$  reaction again indicated the formation of chloromethane. The

GC/MS of the D<sub>2</sub>O reaction solution found only methanol, but the H<sub>2</sub>O solution contained acetic acid, although it did not appear in the NMR spectrum.

### **Supported Pt/Cu Compounds**

Despite many attempts at preparing supported compounds using platinum and copper salts, the resulting compounds have been disappointing. It has been extremely difficult to attain uniform dispersity on the surface of the controlled-pore glass, as evidenced by the uneven coloring of the compounds. Following rotary evaporation, the compounds are not a “free-flowing powder,” as described in the preparation of the Wacker SAP catalyst.<sup>3</sup> Thermogravimetric analysis of the compounds indicated 35-45 weight percent water, which is much higher than expected. The Pt diimine/CPG discussed in Chapter 2 had approximately 2.5 weight percent water, and the as-made Pd/Cu SAP catalyst for Wacker oxidation was 15 weight percent water.<sup>3</sup>

A freshly prepared sample of Pt/CPG was a very light tannish-pink color, but it turns gray overnight, even in a glove box. A “drier” sample, which was pumped on longer by vacuum, didn’t change color overnight. Both the fresh “wet” sample and the “drier” sample turn a darker orangeish/tan color after a TGA run to 950° C in N<sub>2</sub>. The supported copper salt was a very light green/blue color. A drier sample was greener, and the samples with higher loadings of copper were also a brighter green. The samples did not change color by sitting in air, but took on a brighter or more yellow tint after the N<sub>2</sub> TGA run. The Pt-Cu/CPG samples were the most complicated. Following rotary evaporation, there were usually three physically different forms of the sample. A small amount of white flakes fell out of the rotovap flask and turned brown in minutes and were green after sitting overnight. They were found to have only 6 weight percent water. The

most brightly colored product formed a ring around the upper part of the flask while on the rotovap and was 20 weight percent water. The product was primarily lime green, with some brownish areas, but all turned green overnight. With low loadings, it turned blue-gray after TGA run, and with higher loadings, it remained green. The major product had 45 weight percent water. With low loadings, it was initially off-white but turned gray after TGA. Higher loadings yielded pale blue/green powder that did not change color overnight but turned dark blue/gray following TGA. Some samples turned brown within minutes after being removed from the rotovap flask, starting at the edges, and became lime green overnight.

This behavior is very strange and as yet has not been explained. It is likely due to generally poor dispersion. Perhaps the salts need to be supported in an inert environment and the water removal should be done more effectively. Despite the major concerns with the preparation of these catalysts, there are also some issues to be addressed in planning to test the eventual catalysts for reactivity. Work must be done to determine the amount of water required to activate the catalysts for maximum reactivity. It is also likely that there will be an oxygen pressure dependency, as with the Wacker chemistry.<sup>3</sup> Further, product detectability must be addressed. A flow reactor would be the most practical choice as product separation would be extremely difficult in a batch reactor.

## **CONCLUSIONS/FUTURE DIRECTIONS**

The development of a platinum/copper catalyst system able to carry out Shilov chemistry with oxygen as the oxidant will likely prove to be an important step in making the direct hydroxylation of methane practical industrially. Initial studies have used

platinum and copper salts to carry out alkane hydroxylation in solution, and these results served as a good starting point for my own studies towards developing catalysts for methane conversion.

Based on the results from the reactions of ethanesulfonate and ethane, it is evident that the findings of Sen and coworkers<sup>4</sup> are generally reproducible in my reactor system. The reactions were not clean, as other products such as acetic acid and acetaldehyde were also formed, and sometimes in excess of the desired product. Further, the reactor itself did not seem to hold up well under the reaction conditions. But I continued to obtain promising results. Expanding Sen's work to include studies of methanesulfonate and methane demonstrated that the platinum/copper catalyst was also able to readily oxidize C1 alkanes. Both <sup>1</sup>H NMR and GC/MS analysis indicated that methane was being oxidized to methanol.

The generation of methanol is promising and surprising, given that, to my knowledge, this has not been reported for this system. But this issue must be investigated further. There are several factors that could be contributing to this result. There is the possibility of the addition of other elements from the reaction environment, through leaching from the reactor itself or the thermocouple. Perhaps these elements have entered the reaction medium and assisted in catalyzing the production of methanol. By carrying out Electron Microprobe analysis of the solid precipitates recovered after the reaction, I hope to identify any foreign elements present. Once identified, these elements can be tested in a controlled manner for catalytic activity. It is also possible, due to reactor design, that the actual reaction temperature is much higher than the 160° C thermocouple reading. An elevated temperature may be sufficient to drive the hydroxylation of

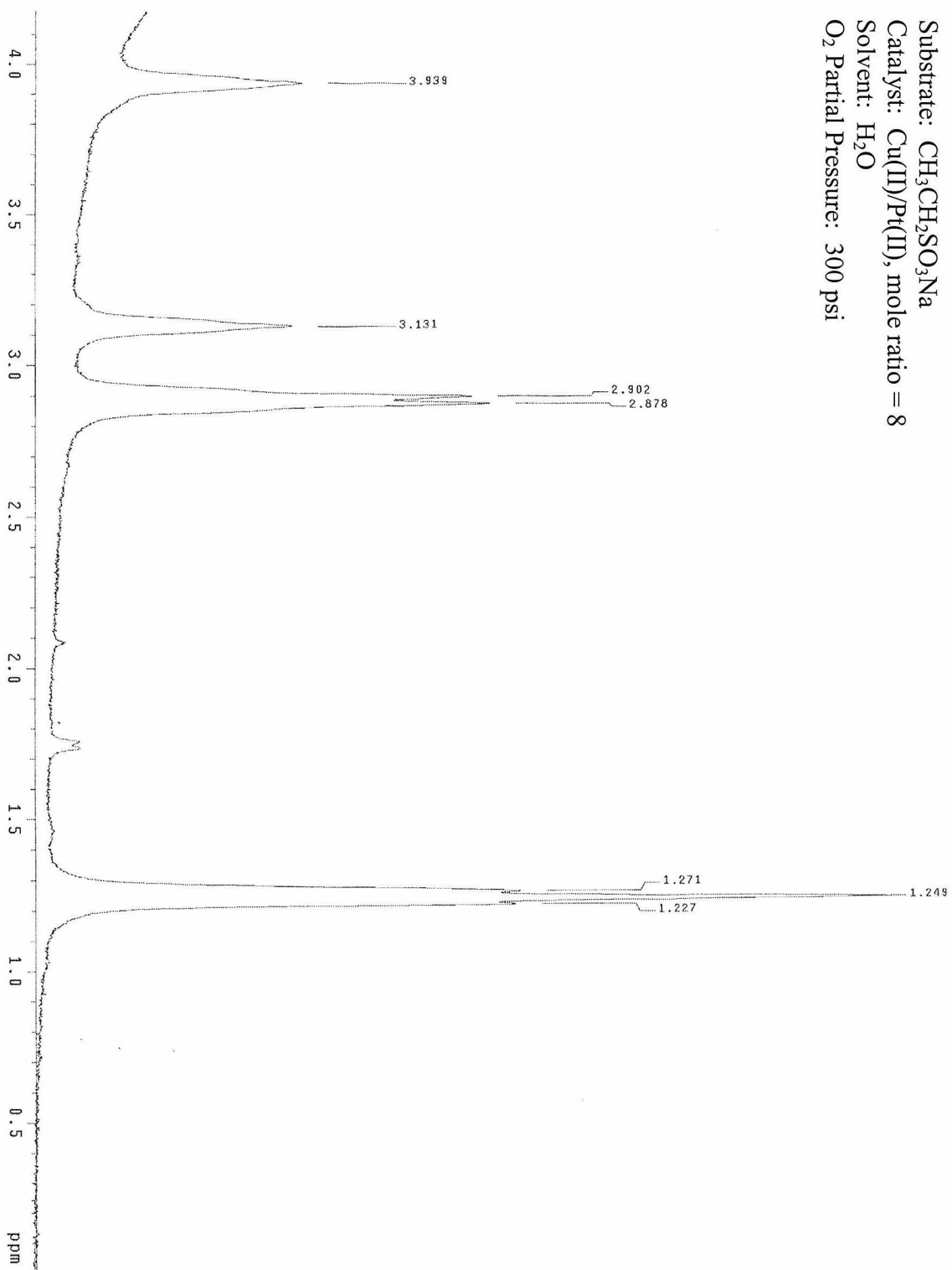
methane. Initial investigations into this factor indicate that the temperature could be as high as 250° C, but this requires further investigation. If true, the temperature control will be modified to maintain a true reaction temperature of 160° C to see how it affects the reactivity. Additionally, methane reactions will be carried out using <sup>13</sup>C-labeled methane. In this way, I will be able to confirm that the methanol is being generated from the methane in the reactor and not from some other source.

Long term goals for this project include optimizing the reaction conditions and the catalyst system used. Further efforts must also be made to identify all the products being generated in these reactions, and quantification of results would be beneficial as well. Eventually, this catalyst system will likely be developed into an SAP catalyst and tested in a flow reactor for activity towards alkanes.

**REFERENCES**

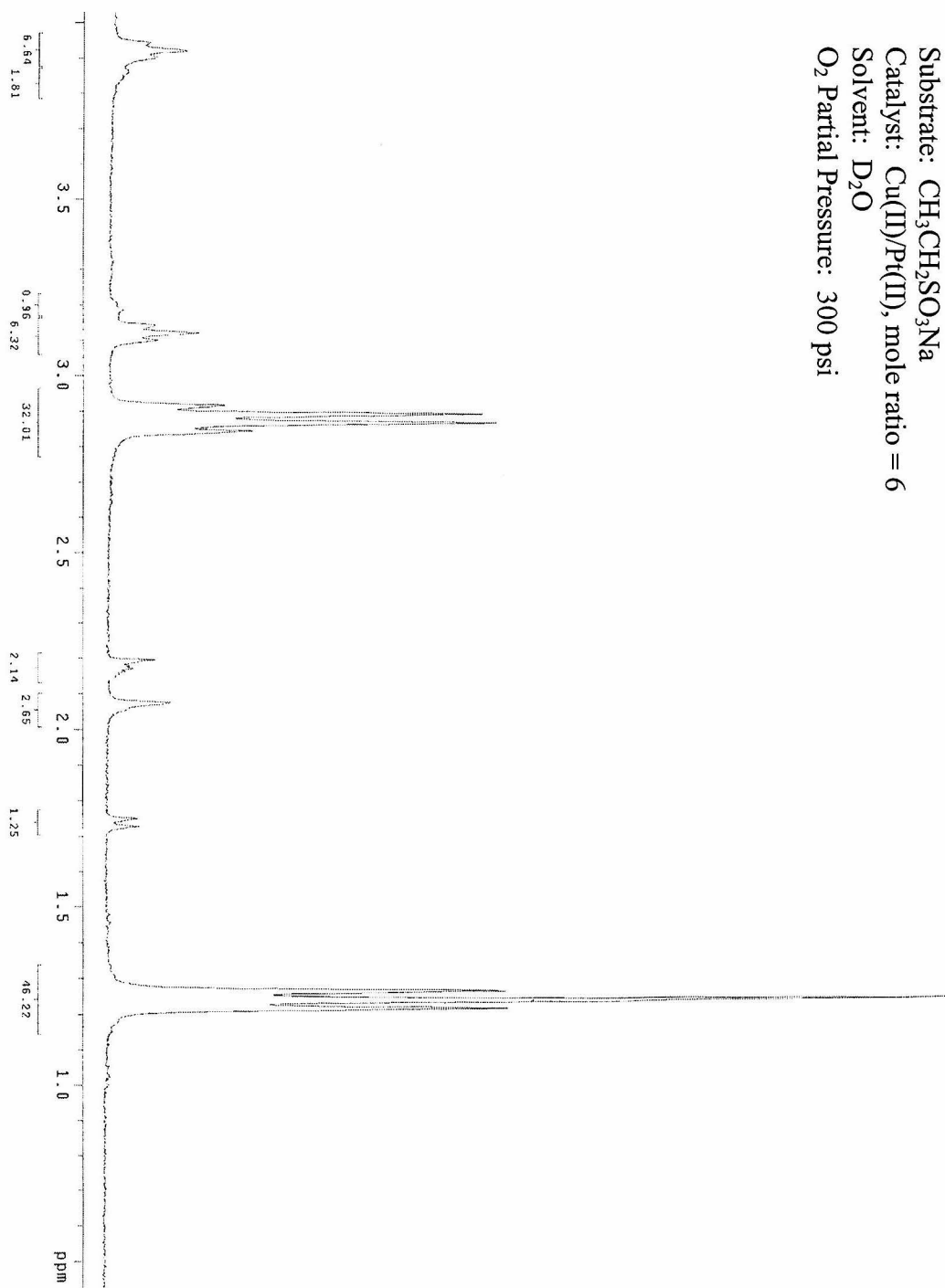
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2. Rostovtsev, V.V.; Labinger, J.A.; Bercaw, J.E.; Lasseter, T.L.; Goldberg, K.I. *Organometallics*, **1998**, *17*, 4530-4531.
3. Arhancet, J.P.; Davis, M.E.; Hanson, B.E. *Catal. Lett.*, **1991**, *11*, 129-136.
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## SPECTRA

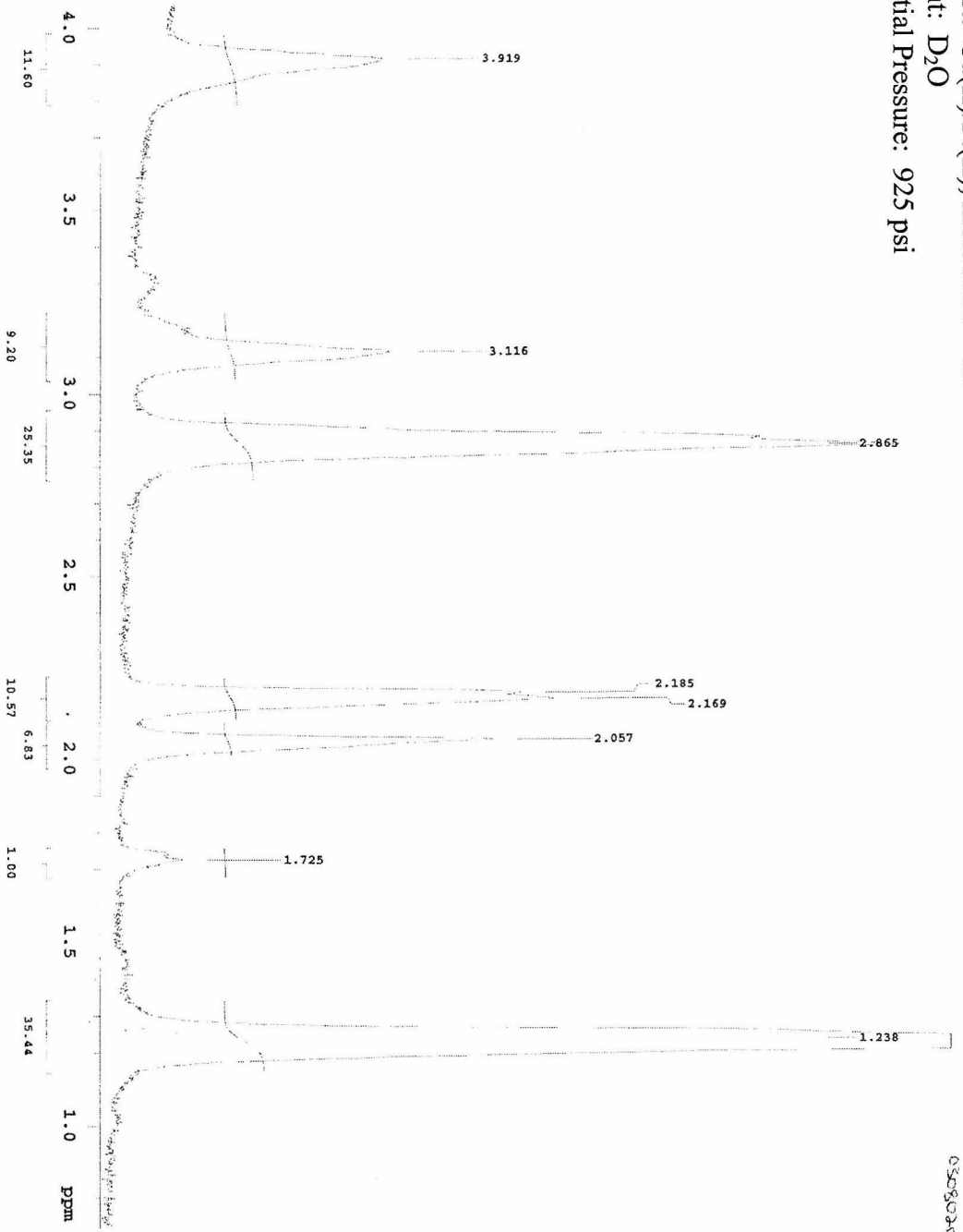




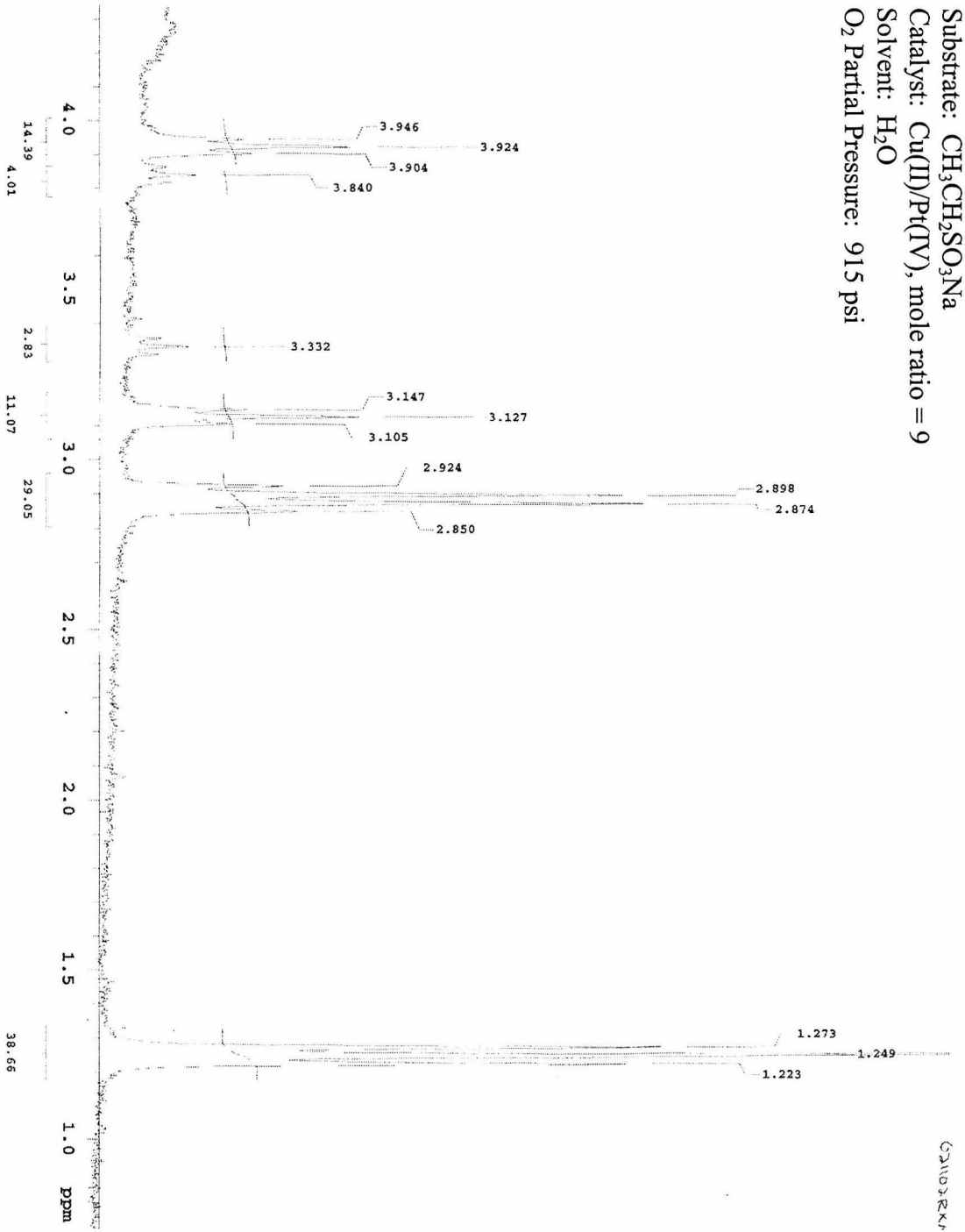
Substrate:  $\text{CH}_3\text{CH}_2\text{SO}_3\text{Na}$   
Catalyst:  $\text{Cu(II)/Pt(II)}$ , mole ratio = 6  
Solvent:  $\text{D}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 300 psi



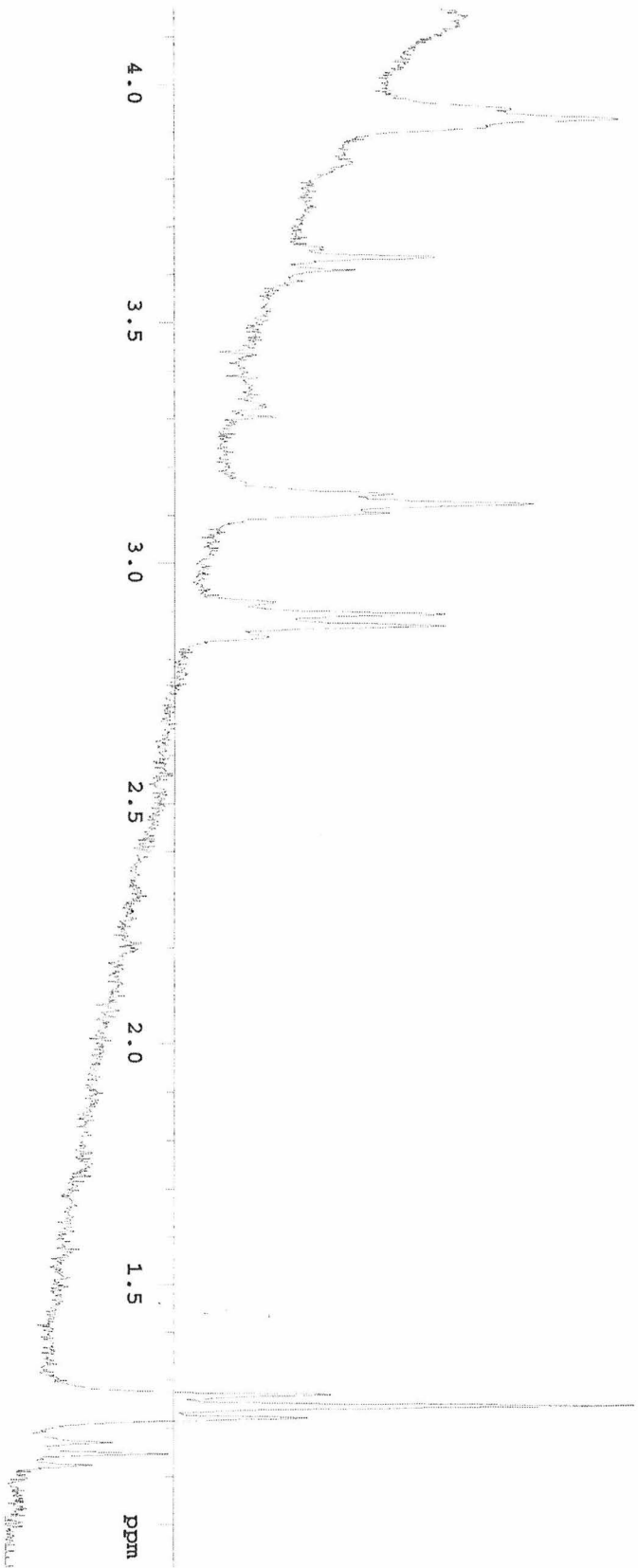
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Catalyst:  $\text{Cu(II)/Pt(II)}$ , mole ratio = 6.5  
Solvent:  $\text{D}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 925 psi



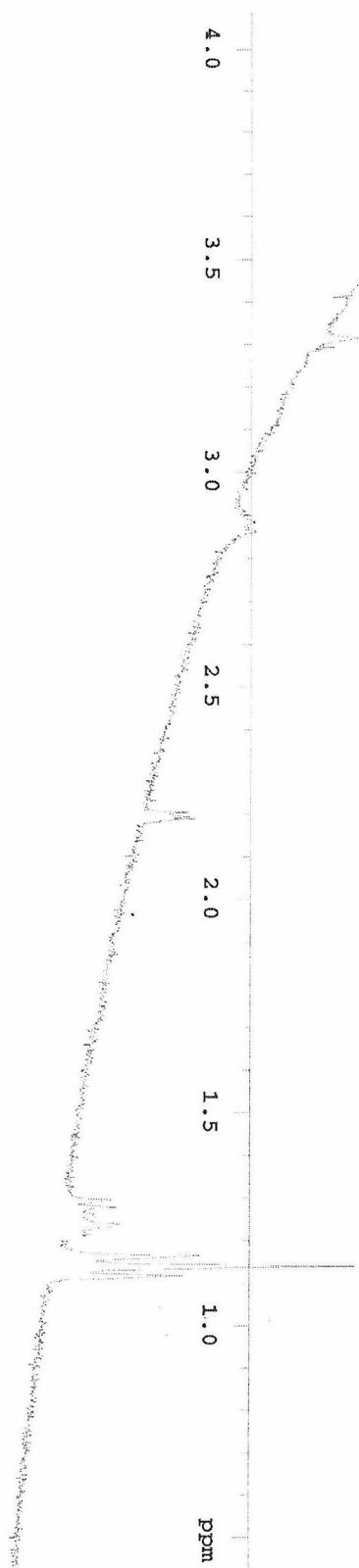
Substrate:  $\text{CH}_3\text{CH}_2\text{SO}_3\text{Na}$   
Catalyst:  $\text{Cu(II)/Pt(IV)}$ , mole ratio = 9  
Solvent:  $\text{H}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 915 psi



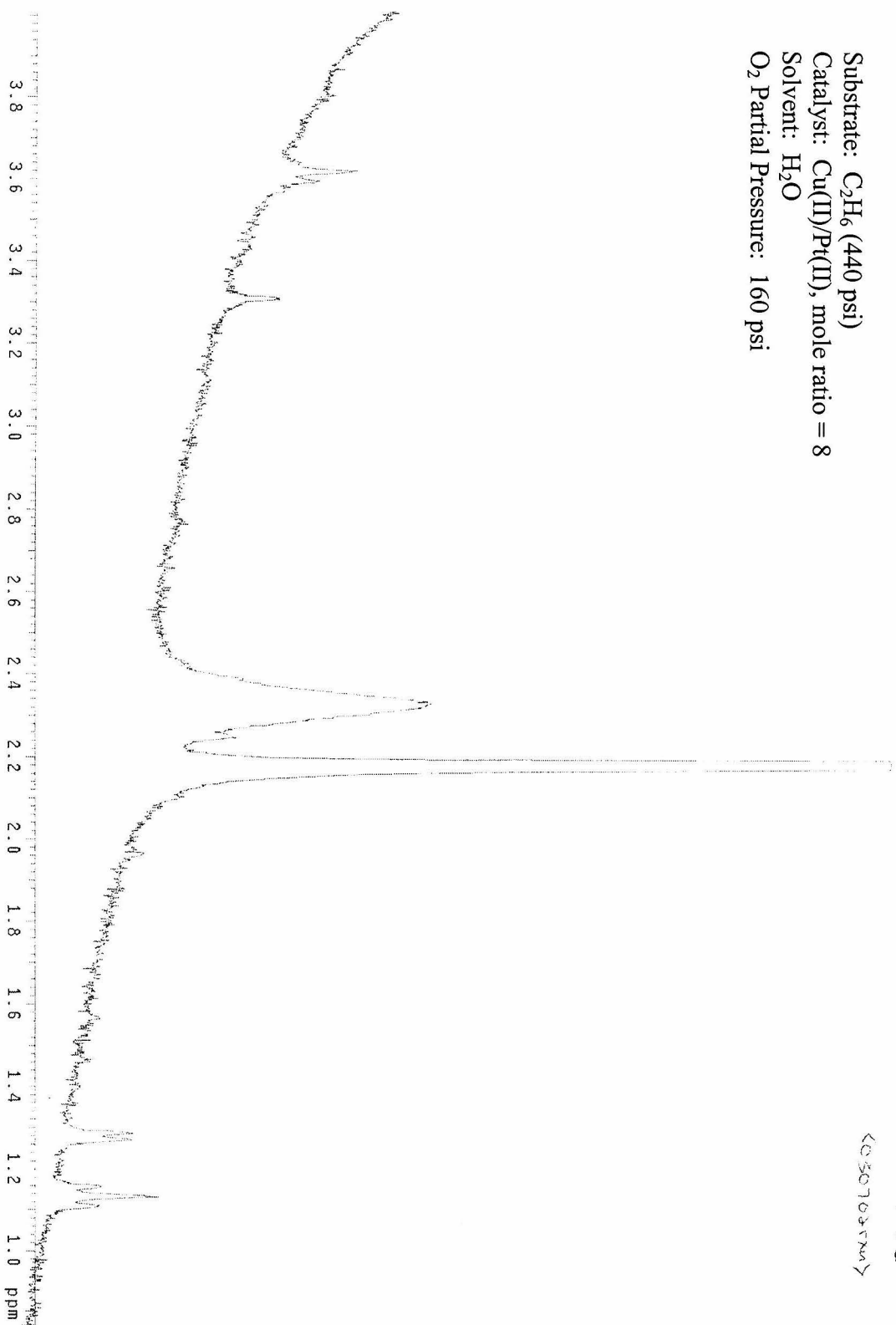
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Catalyst:  $\text{Cu(II)/Pt(II)}$ , mole ratio = 10  
Solvent:  $\text{H}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 145 psi



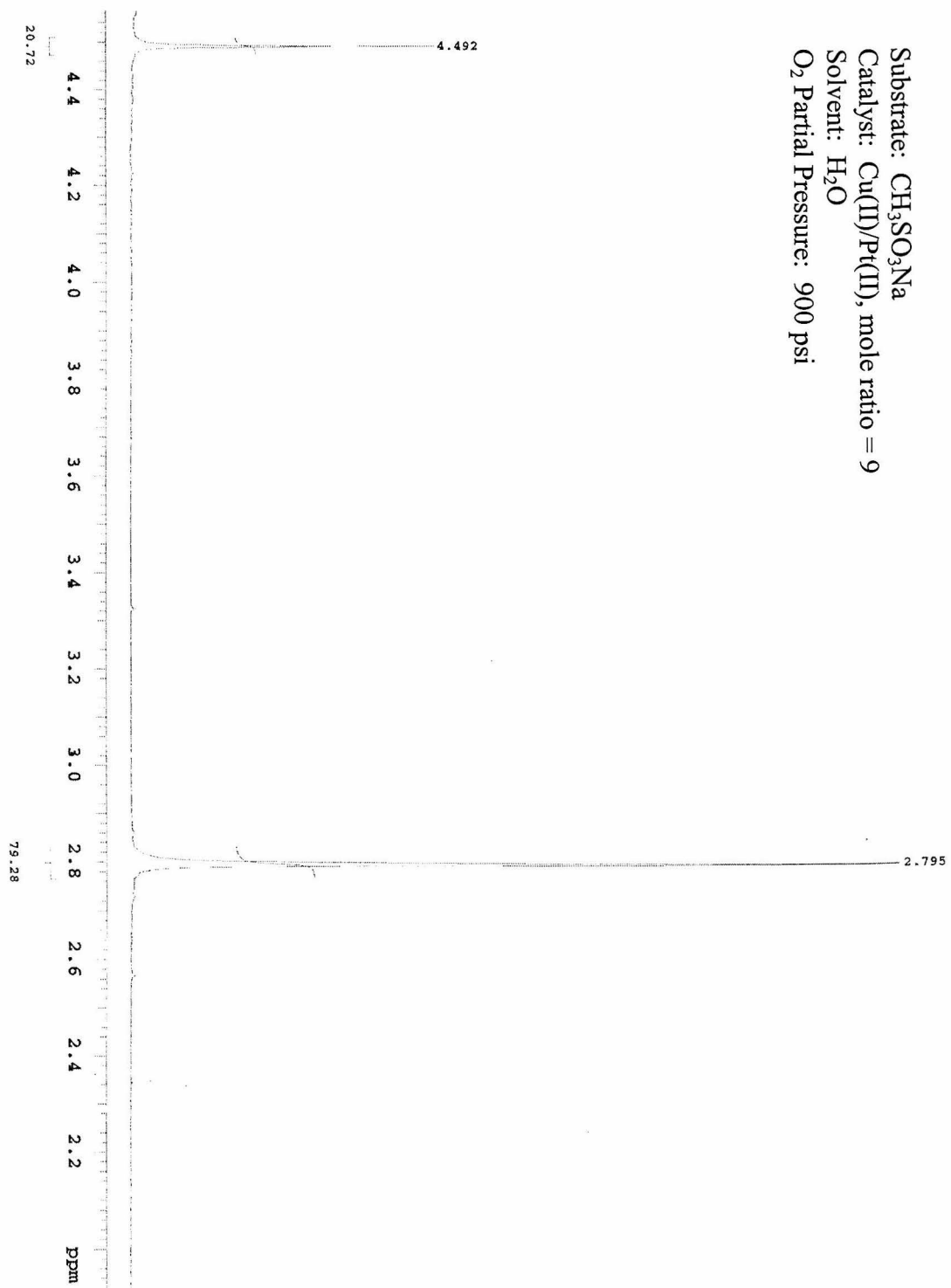
Substrates:  $\text{CH}_3\text{CH}_2\text{SO}_3\text{Na}$ ,  $\text{C}_2\text{H}_6$  (440 psi)  
Catalyst:  $\text{Cu(II)/Pt(II)}$ , mole ratio = 9  
Solvent:  $\text{H}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 175 psi



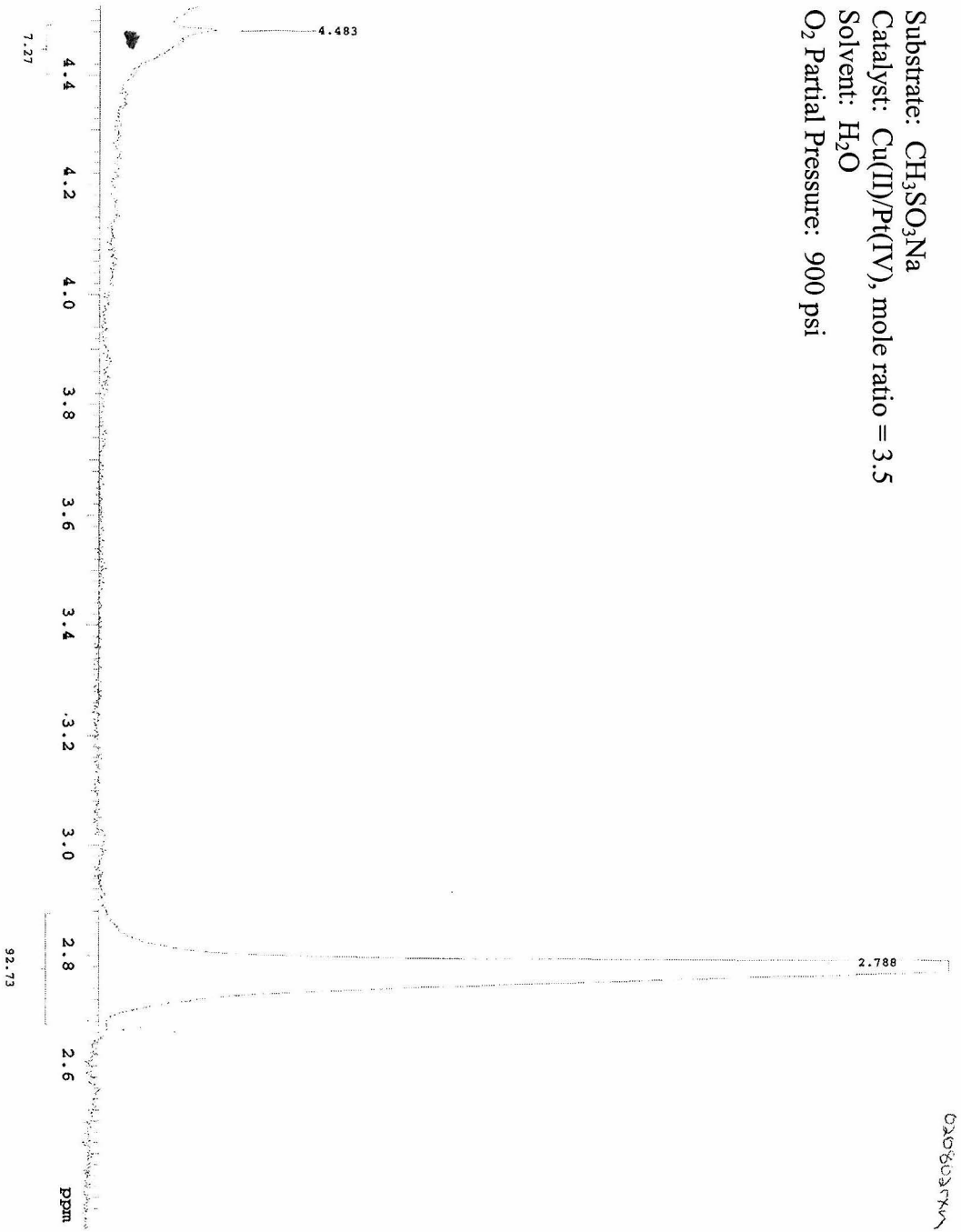
Substrate:  $C_2H_6$  (440 psi)  
Catalyst: Cu(II)/Pt(II), mole ratio = 8  
Solvent:  $H_2O$   
 $O_2$  Partial Pressure: 160 psi



Substrate:  $\text{CH}_3\text{SO}_3\text{Na}$   
Catalyst:  $\text{Cu(II)/Pt(II)}$ , mole ratio = 9  
Solvent:  $\text{H}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 900 psi

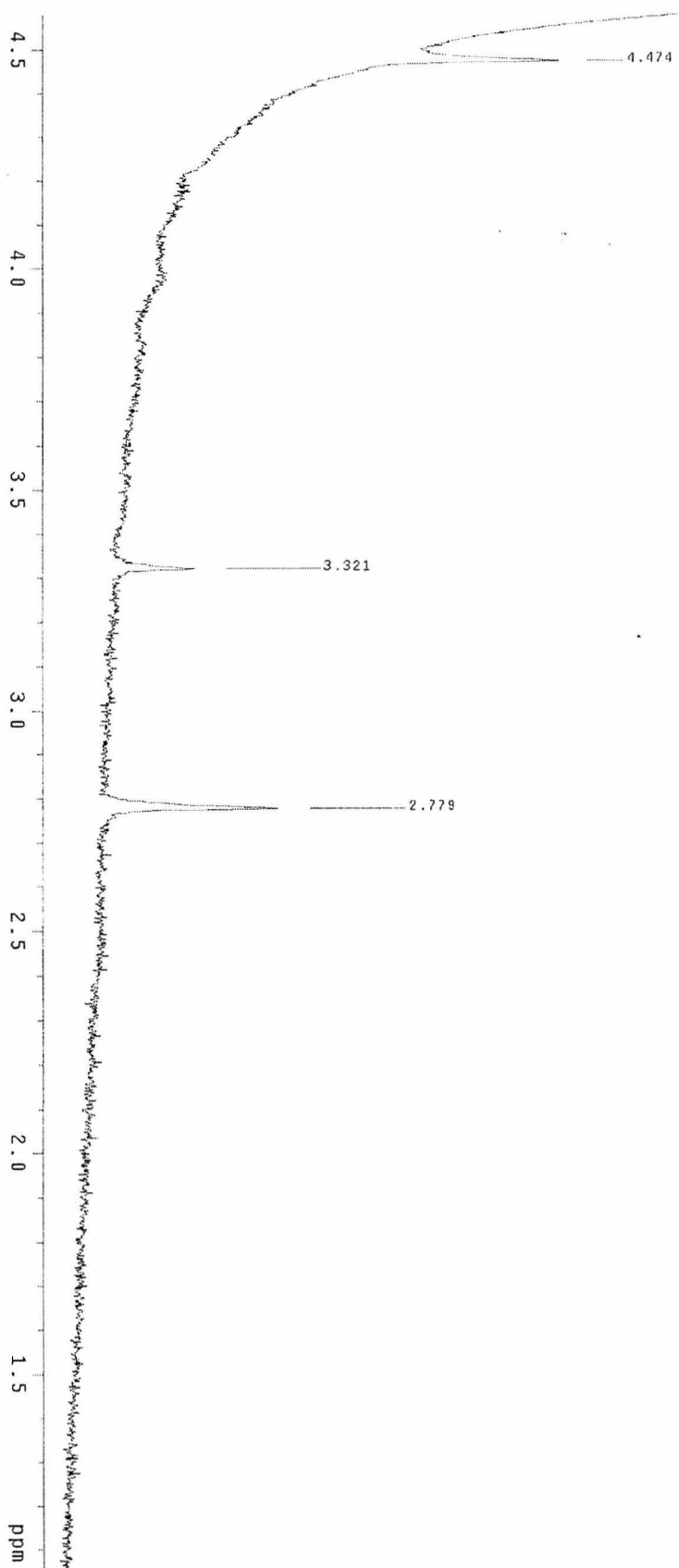


Substrate:  $\text{CH}_3\text{SO}_3\text{Na}$   
Catalyst:  $\text{Cu(II)/Pt(IV)}$ , mole ratio = 3.5  
Solvent:  $\text{H}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 900 psi

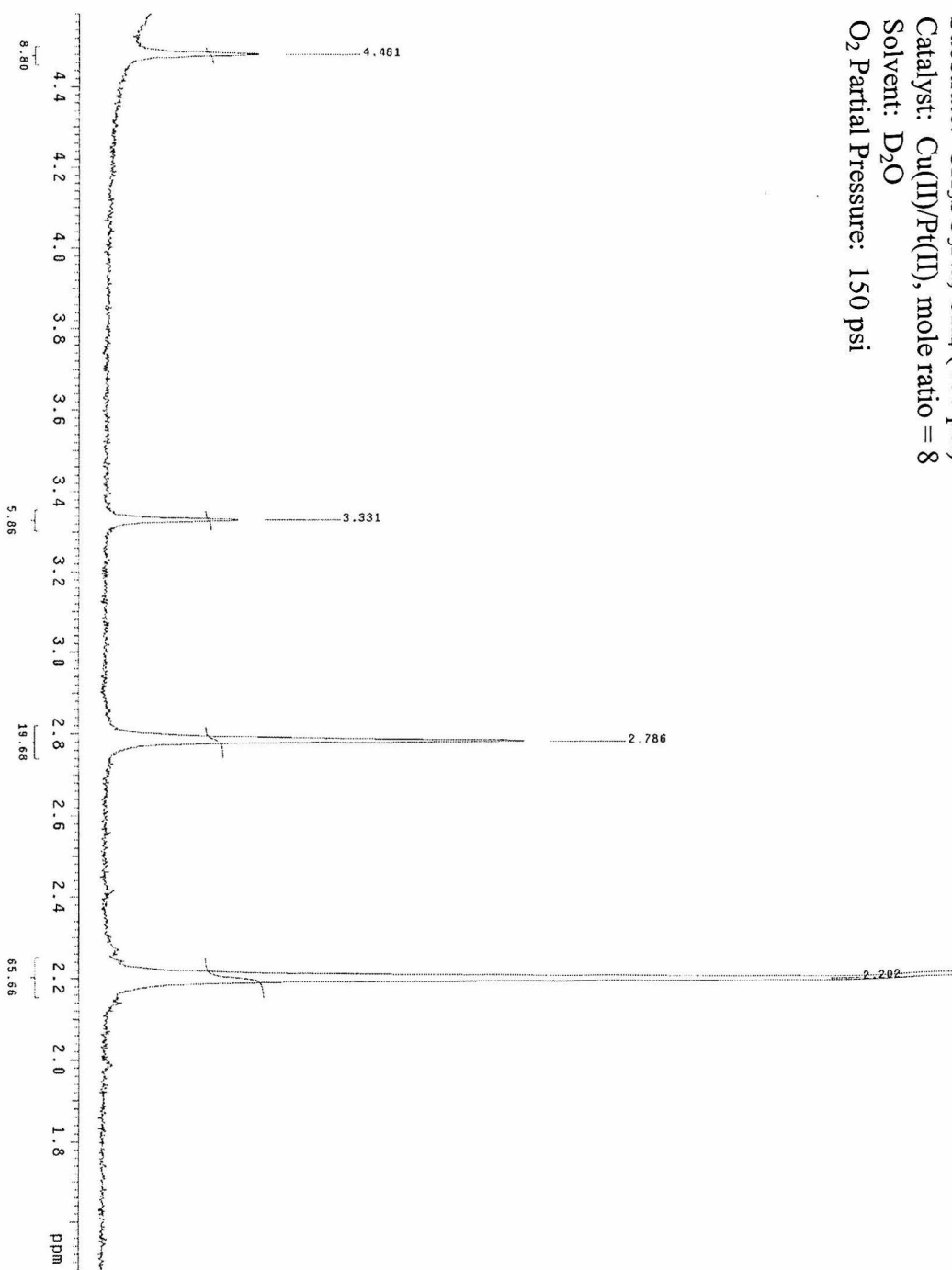




Substrate:  $\text{CH}_3\text{SO}_3\text{Na}$ ,  $\text{CH}_4$  (400 psi)  
Catalyst:  $\text{Cu(II)/Pt(II)}$ , mole ratio = 9  
Solvent:  $\text{H}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 170 psi



Substrate:  $\text{CH}_3\text{SO}_3\text{Na}$ ,  $\text{CH}_4$  (400 psi)  
Catalyst:  $\text{Cu(II)/Pt(II)}$ , mole ratio = 8  
Solvent:  $\text{D}_2\text{O}$   
 $\text{O}_2$  Partial Pressure: 150 psi



Substrate: CH<sub>4</sub> (400 psi)  
Catalyst: Cu(II)/Pt(II), mole ratio = 9  
Solvent: D<sub>2</sub>O  
O<sub>2</sub> Partial Pressure: 150 psi

